Pre-Harvest Water Quality in Ephemeral Streams in Missouri Ozarks Forests

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The undersigned, appointed by the Dean of the Graduate Faculty, have examined a thesis entitled

"PRE-HARVEST WATER QUALITY OF EPHEMERAL STREAMS IN MISSOURI OZARK FORESTS"

Presented by Abraham Smith,

a candidate for the degree of Master of Science and hereby certify that in their opinion it is worthy of acceptance

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**ABSTRACT**

Forests are the origin for 80% of the fresh water utilized in the United States.  Timber harvesting has been widely blamed for the degradation of such water stores. In order to reduce the potential for such adverse effects, the Missouri Department of Conservation (MDC) developed a best management practice that leaves a riparian buffer next to streams to reduce the possibility of water quality degradation.  The purpose of this study is to quantify water quality in upland forested watersheds before harvesting commences in order to provide a baseline for comparison with post-harvest water quality analyses.  Water monitoring occurred on 15 sites in and around Current River and Angeline Conservation Areas in Missouri, USA.  Water samples were collected from in-stream water samplers located in the ephemeral drainage way and (2) hillslope samplers located on slopes adjoining the ephemeral drainage way.  The water samples were tested for total phosphorous, soluble reactive phosphorous, total nitrogen, nitrate, ammonia, calcium, magnesium, potassium, total suspended solids, total volatile suspended solids, pH, and electrical conductivity.  The time period of sample collection began in October 2004 and lasted to January 2006.  This time period yielded nearly 384 samples.  The baseline levels for all constituents have been quantitatively determined by utilizing the "three sigma method" which incorporates data from 99.87% of all values recorded for the species of interest.  The following baseline values were established: pH was 8.3, electrical conductivity was 200 us/cm, TSS was 0.5 g/L and TVSS was 0.2 g/L, Ca was 13 mg/L and Mg was 10 mg/L, K was 10 mg/L, TP was 1.3 mg/L and SRP was 1.1 mg/L, total nitrogen was 5.8 mg/L and nitrate and ammonia concentrations were 1.3 and 1.6 mg/L respectively.  All parameter concentrations were found to have strong seasonal trends, and varied greatly from site to site.

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**Chapter 1 – Introduction**

**1.1 Overview**

Forested areas are the source of more than 80 percent of all fresh water (MDC, 1997). There is concern that timber harvest operations might adversely affect the quality of the surface water from forest sources. The forest vegetation not only provides some control over the rate of water discharge but it also protects the watershed and, thus, the water quality against the effects of erosion, sedimentation, leaching of nutrients, overland flow (Pope, 1977). Harvesting of a forest canopy disrupts the annual circulation of nutrients. The harvest takes away some or all of the many years accumulation in the aboveground stand (Stone, 1975). Such removal of crown allows for mass movement more readily and with the addition of skidder trails this movement is compounded (Doisy, 2000).

The Current River in southern Missouri is nationally renowned for fresh water resources obtained from forest runoff (MDC, 1997). The Missouri Department of Conservation (MDC) conducts timber harvesting on state lands surrounding the Current River to maintain a diverse selection of tree and plant species, preserve wildlife habitat, and to produce commercial products (MDC, 1997). Potential, pollution from this silvicultural practice is referred to as a non-point pollution source and as such must follow the statutes of the Clean Water Act of 1977 and the Clean Water Act of 1987 (EPA, 1987). The Clean Water Acts dictate that silviculture activities cannot adversely affect the water that leaves forested watersheds, as they may also negatively impact larger bodies of water. In order to ensure that the effluent from timber harvest sites is not degraded, MDC enforces a best management practice (BMP) of leaving a riparian buffer

zone (RBZ), also referred to as a streamside management zone (SMZ), to negate any detrimental effects. The Missouri Department of Conservation developed its BMP for silvicultural practices in 1987. The RBZ constitutes a strip of vegetation that is conserved in order to improve water quality through various processes depending on the pathway of the flow of water through the buffer. In the case of surface flow, the vegetative cover impedes flow, causing suspended solids to sediment, and acts as a sink for nutrients. The riparian buffer zones are placed alongside perennial and ephemeral drainage ways as these are main pathways for the movement of water.

An investigation into the efficacy of MDC's best management practice is underway to insure the viability of the surrounding ecosystem and address a negative public perception of timber harvesting. The Ozark Timber Harvest study is a collaborative effort of MDC, the Missouri Department of Natural Resources (MDNR), United States Department of Agriculture Forest Service (USDA), and the Institute for Interdisciplinary Geotechnics (I2G). It is the task of I2G to quantitatively determine the impact of timber harvesting, specifically regenerative oak clear cuts, on water quality in ephemeral streams in the Missouri Ozark Highlands.

**1.2 Overall Goals**

The main goal of the project is to determine the efficiency of Missouri Department of Conservation's best management practice as it pertains to protecting the water quality in ephemeral drainage ways. A second objective is to ascertain if other methods should replace or be used in conjunction with the RBZ to better protect the water quality. A final objective is to improve our understanding of the varying erosional and hydrological processes of ephemeral channels next to harvested areas.

**1.3 Methodology**

Fifteen study sites were selected for the project. The study sites are located in Shannon and Reynolds counties in southern Missouri (Figure 1.1)



**Figure 1.1 Location of the Study Sites in Shannon and Reynolds Counties, Missouri with Regard to the University of Missouri-Columbia**

The study sites are highlighted by the shaded box and the star illustrates the University of Missouri-Columbia campus. The fifteen sites are spread throughout the Angeline and Current River Conservation Areas, owned by the State of Missouri and operated by the Missouri Department of Conservation (Figure 1.2 and Figure 1.3). The sites share similar characteristics. Each site consists of a central ephemeral stream and its drainage basin. The basins are characterized as highly dissected and steeply sloped. Ten of the 15 sites will be harvested. The time of harvest depends on a timetable set by MDC. For all

harvest sites, one to two years of pre-harvest data have been collected and up to three

years of post harvest data will be collected.
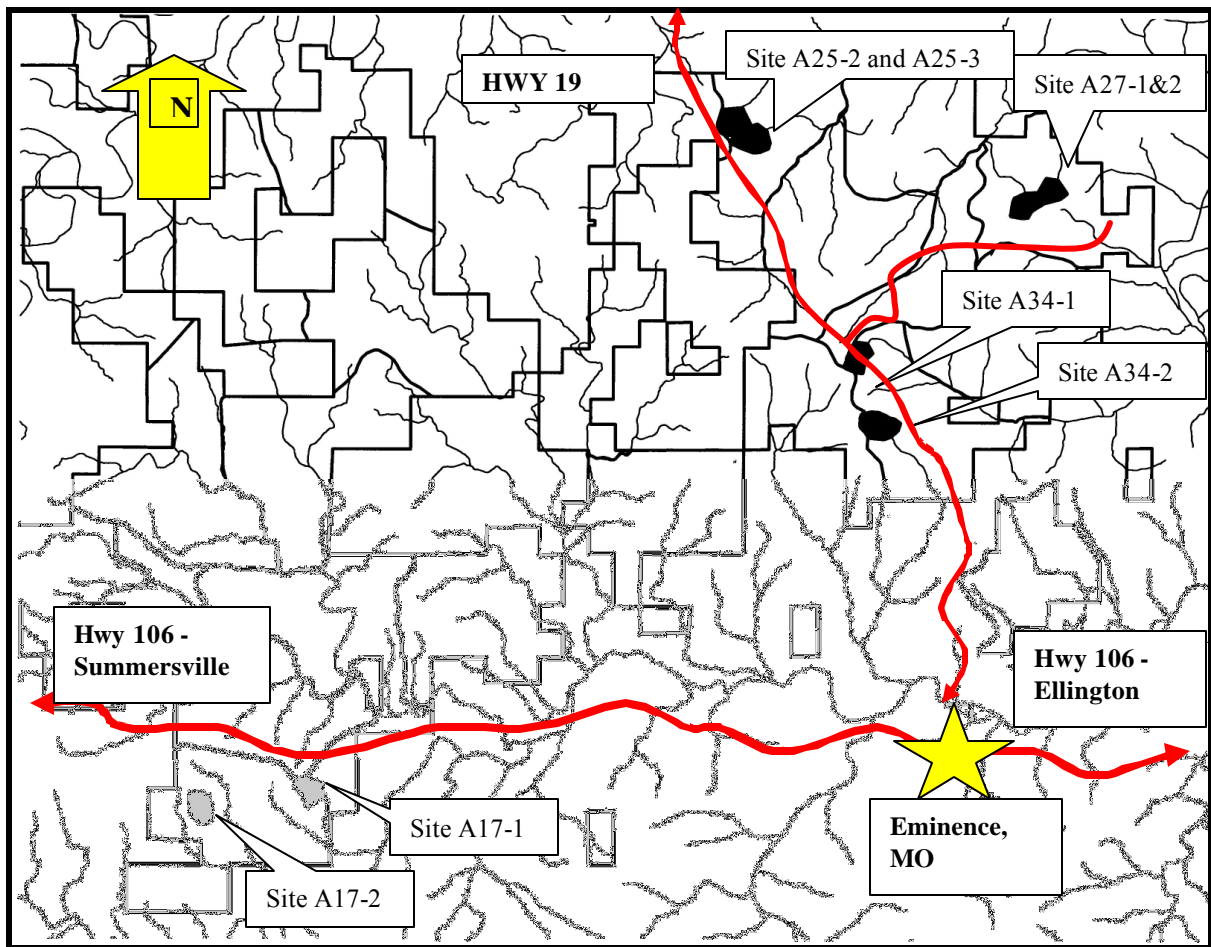
**Figure 1.2 Sites Located in the Angeline Conservation Area operated by the Missouri Department of Conservation**
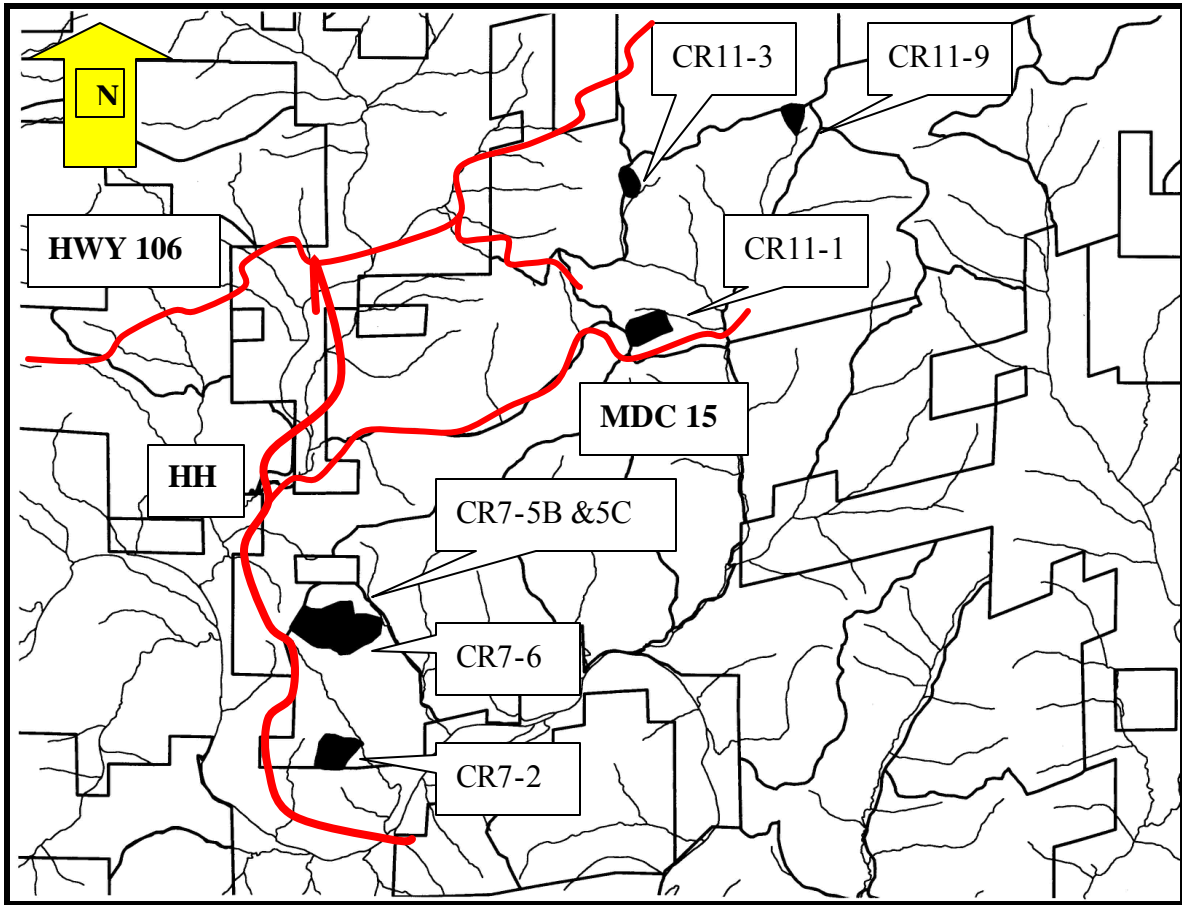
**Figure 1.3 Sites Located in the Current River Conservation Area operated by the Missouri Department of Conservation**

Five sites will not be harvested and will serve as control sites.  With one exception, only one aspect of each site will be harvested.  Figures 1.2 and 1.3 pinpoint the location of the 15 sites and it can be observed that many of the sites are clustered together to minimize spatial and microclimatic variability.

Two instrumentation schemes are being used - "extensive" and "intensive". Intensively monitored sites have more sample collection apparatuses.  Of the sites that are intensively monitored, three are cut sites and one is a control site.  In order to analyze the influence of the riparian buffer zone, water samples must be collected.  The collection of these samples is accomplished with in-stream bottle samplers and hillslope samplers (Bunger, 2005).  The in-stream bottle samplers are placed in the main ephemeral channel at the head of the channel; any point in the length of the channel where another first order ephemeral stream intersects the main ephemeral channel, and at the downstream end of the channel.  Ninety-one in-stream bottle samplers have been installed.  Hillslope samplers were placed with regard to concavities and convexities in the landscape. Multiple hillslope samplers were placed on the harvest aspects of sites; and one trap was placed on the control side of the site.  A total of 69 hillslope samplers were installed. A typical site instrumentation outline can be seen in Figure 1.3.
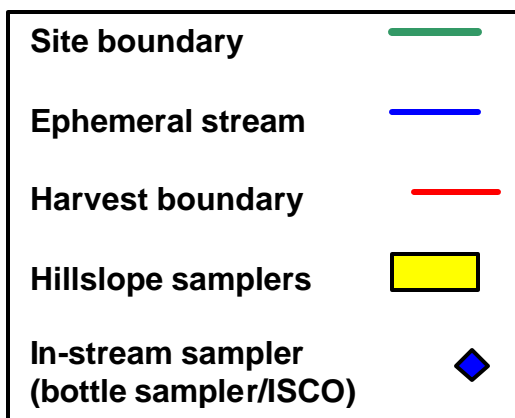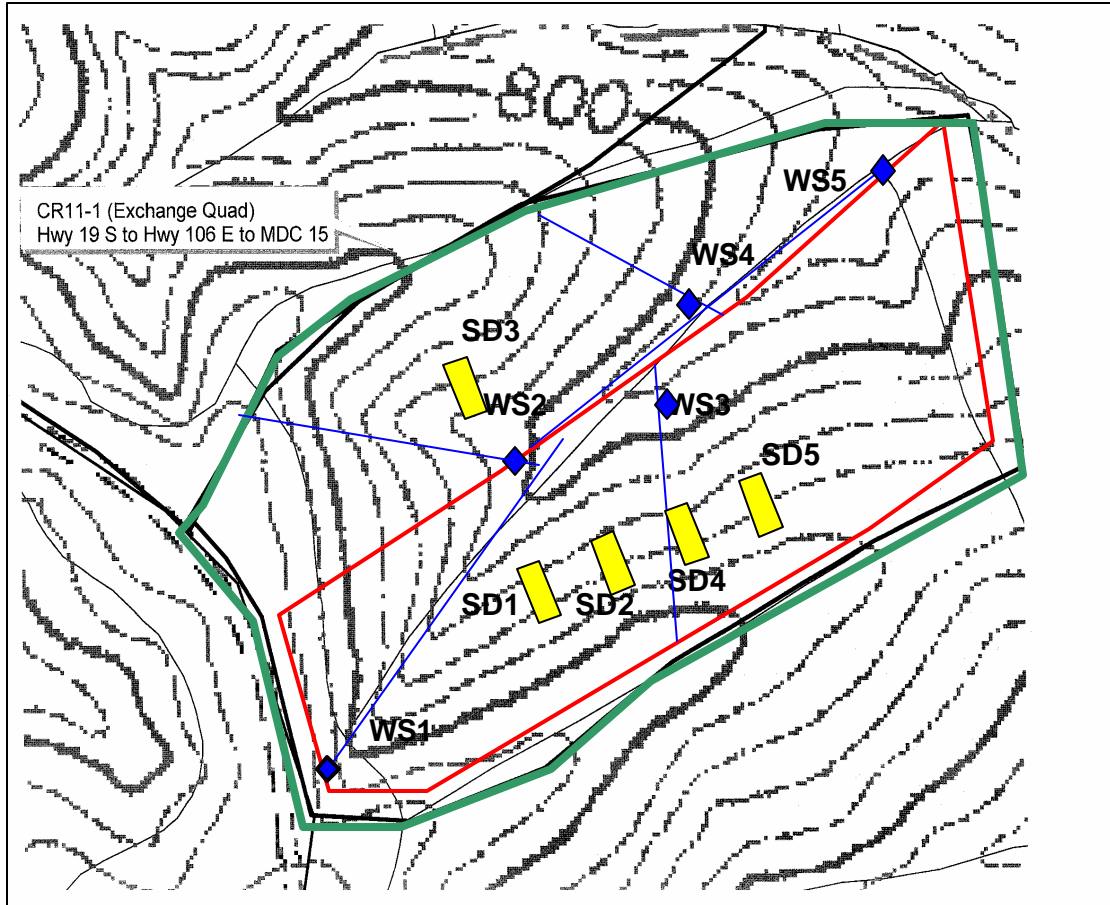
**Figure 1.4 Typical site outline of instrumentation and harvest with accompanying key (Bunger, 2005)**

**1.4 The Ozarks**

The study area is located in the Current River Hills subsection of the Ozark Highlands. This subsection consists of a hilly to deeply dissected landscape due to the Current, Black, and Eleven Point drainage basins (Nigh and Schroeder, 2002). Dolomite, sandstone, and chert from the Roubidoux, Gasconade, and Eminence formations are the dominant bedrock materials. Ground in this upland region is generally weathered Alfisols and Ultisols and are rocky due to chert fragments that formed from multiple parent materials, including layers of hillslope sediments, residuum, and loess. Due to a large amount of dolomite, karst features are common and include caves, springs, seeps, and sinkholes. Second-growth forests dominate the landscape, with cleared land in valley bottoms. These characteristics are attributed to previous land use that included intense timber harvesting. The timber harvesting has been hypothesized as a main reason for the formation of the hillslope sediments (Daniels and Hammer, 1992). Currently much of the area is in public lands (Nigh and Schroeder, 2002). Mueller (2006), unpublished report, describes the Ozark study sites for variables including: elevation, topography, landtype, slope, aspect, and geology.

**1.4.1 Ozark Climate Regime**

The Ozark Highlands is classified as a humid-continental climate. Mean annual precipitation ranges from 43 inches in the north to 48 inches in southern parts of the Ozarks (Nigh and Schroeder, 2002). The wettest months are from March to May, but average precipitation amounts also peak in August. Fifty-six percent of the annual precipitation occurs during the six warmer months of the year. Yearly temperatures vary from a mean temperature of 20 degrees F in January and a maximum mean daily

temperature of 90 degrees F in July.  Significant microclimatic variations occur locally because of the high relief of the land (Nigh and Schroeder, 2002).

**1.4.2 Ozark Geology**

The Current River Hills subsection lies on the southeastern flank of the broad Ozark uplift.  Local relief throughout most of the subsection is high, ranging from 200 to 600 feet (Nigh and Schroeder, 2002).  The study area is underlain by nearly horizontal, cherty, massively bedded dolomites of the Gasconade and Eminence formations.  In some areas, Roubidoux formation sandstones exist on ridge tops.  All materials in the thick sequence of carbonate rocks are soluble and create karst topography, including some very large springs and caverns, sinkholes, and dry valleys (Nigh and Schroeder, 2002).  A general cross section of bedrock geology of the region is shown in Figure 2.1.
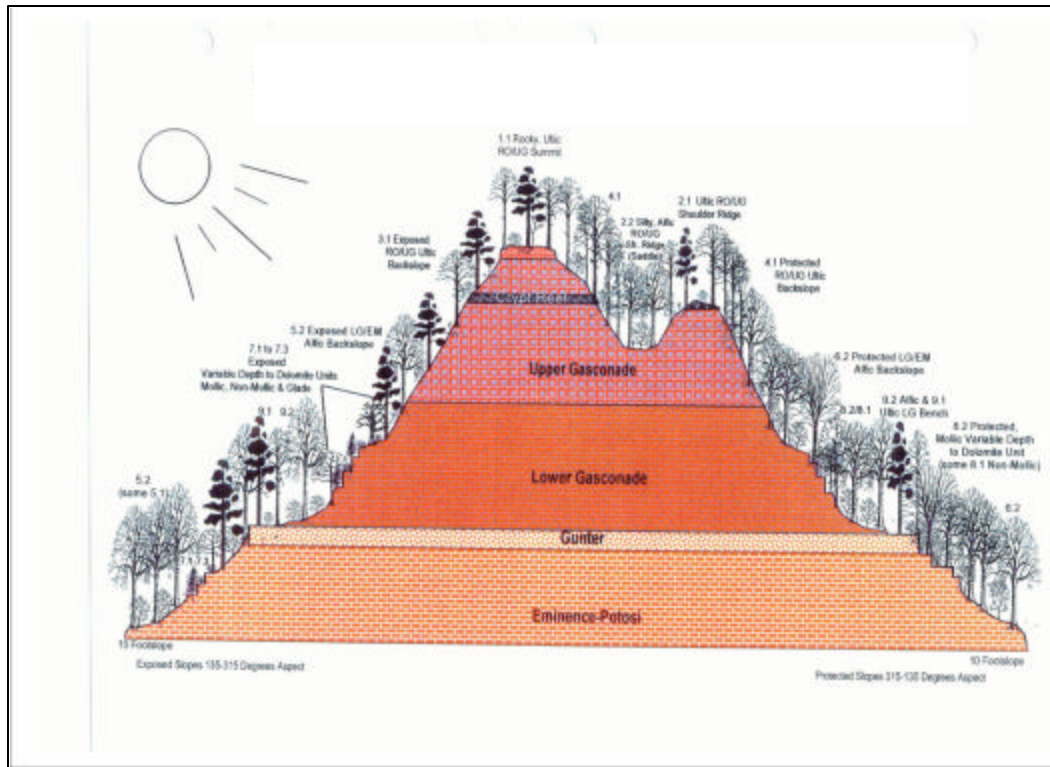
**Figure 1.5 Typical bedrock geology underlying the study area (from Nigh, 2000)**

The Roubidoux formation is the youngest formation and thus exists primarily on summits, high ridges, and upper backslopes (Nigh and Schroeder, 2002). As a result of its location, this formation is highly weathered and most of its dolomite deposits have eroded leaving behind cherty soils over sandstone or chert bedrock. Soil developed within this formation usually form Ultisols (low base saturation), are moderate in depth, and are well drained and exist with discontinuous fragipans. Parent materials of such soil include hillslope sediments over residuum.

The Gasconade formation exists just below the Roubidoux formation. This formation is separated into three sections: upper Gasconade, lower Gasconade, and is underlain by the Gunter Sandstone Member.

The upper Gasconade begins right below the Roubidoux formation and is approximately 140 feet thick. It includes the Cryptozoan Reef Chert bed, the main consistency for many structural benches (Nigh and Schroeder, 2002). This stratum boasts large deposits of dolomite that are usually cherty. Soil developed in this stratum are usually Ultisols, are frequently deep, and well drained. This stratum also contains intermittent fragipans.

The lower Gasconade is characterized by fine dolomites with a lesser percentage of chert content. It is analogous to the Van Buren strata defined by Bridge (1930) and Thompson (1995). Soil formed within this formation is Alfisols.

The Eminence formation underlies the Gunter Sandstone Member of the Gasconade formation. It is characterized by Cambrian-aged dolomite and variable chert content. Similar to the lower Gasconade, the soil produced within the Eminence

formation is likely Alfisols. The soil varies in depth from shallow, bedrock at the surface, to deep, 60 inches below the surface (Bridge 1930; Thompson, 1995).

### 1.4.3 Ozark Topography/Soils/Vegetation

The soils in the Ozarks are closely related to bedrock lithology and landscape position and are formed primarily in loess, hillslope sediments, residuum, or gravelly alluvium (Kabrick et al., 2000). Most of the soils in the subsection are highly weathered and range from shallow unconsolidated materials over bedrock to a very deep soil in hillslope sediments and/or residuum.

The region is at the center of the largest block of forest in the Ozarks and one of the largest in the Midwest (Nigh and Schroeder, 2002). Natural vegetation consists mainly of second-growth oak-hickory and oak-short leaf pine forests and woodlands, oak savannas, and glades (Kabrick et al., 2000). Bottomland and mixed upland hardwood forests occur in large valleys and on adjacent side slopes. The region supports a substantial timber industry (Nigh and Schroeder, 2002).

### 1.4.4 Ozark Hydrology

The Current River Hills subsection lies within the Black River, Current River and Eleven point drainage basins. Gradients are relatively steep; and streams carry very little suspended sediment and have the reputation for being exceptionally clear (Nigh and Schroeder, 2002). This complex underground distribution system often produces erratic and often seemingly inconsistent runoff patterns from most of the region's major drainage basins during certain seasons (Settergren, 1972). Losing stretches are common in ephemeral drainage ways located higher in the landscape.

**1.5 Specific Objectives**

The principal objective of the work described in this thesis is to quantify the baseline (pre-harvest) water quality concentrations for various parameters. The baseline values will form a reference point to compare with water quality parameters measured after timber harvesting. The baseline values will be established by using the Three Sigma Method (Duncan, 2002). Subtasks of this objective include the selection of water quality parameters to be quantified, and the establishments of methods to best analyze data collected from the field.

**1.6 Scope**

The scope of this thesis includes the collection and analysis of samples collected from October of 2004 through January 2006. Three hundred and eighty-four samples were collected in this time frame. The samples were analyzed for 12 parameters: pH, electrical conductivity, nitrate ($NO_3$), ammonia ($NH_3$-N), total nitrogen (TN), soluble reactive phosphorous (SRP), total phosphorous (TP), calcium (Ca), magnesium (Mg), potassium (K), total suspended solids (TSS), and total volatile suspended solids (TVSS). The parameters were selected for their importance to a forested watershed, their potential to negatively impact water quality, and as indices to better understand the erosional and hydrological processes of ephemeral channels next to harvested areas.

**1.7 Thesis Outline**

Pertinent literature has been reviewed in Chapter 2. All laboratory techniques are described in Chapter 3, Methods and Materials. Chapter 4 includes the presentation and discussion of the water quality data. Practical implications of the findings are described in Chapter 5. Conclusions are presented in Chapter 6. Recommendations are made in

Chapter 7. Chapter 8 contains a list of relevant references. The Appendix includes (1) data sets relevant to the thesis, (2) All lab analysis data is presented, (3) The results of a degradation study and a machine comparison study, (4) Standard operating procedures for laboratory methodology, (5) Methods of detection limits as well as the detection limits for the analytical analyses, (6) A comparison of samples collected from grab samples with samples collected from instrumentation, (7) Frequency distributions of all 12 parameters, and (8) Aluminum and iron results for thirty samples.

**Chapter 2 - Literature Review**

**2.1 Introduction**

"The shear complexity of evaluating the downstream effects of a combination of management practices, on sites of varying topography and soil type, and over different time periods is overwhelming" (Holtje, 1977). The forest ecosystem is a unique, dynamic community created by a myriad of interconnected factors that simultaneously shape the ecosystem. Climatic factors such as precipitation amount and yearly temperature range are the primary factors for the formation of a forested landscape. The topography changes as climatic conditions intermix with the pre-existing geology. As the landscape evolves, unique soil conditions are formed. With the formation of nutrient rich soil, vegetation and later differing organisms begin to interplay with the formation of a forested ecosystem (Stone, 1975). The Ozark landscape is a temperate, mixed hardwood forest that has developed over millennia and as such is a complex system that has many interdependent cycles and relationships. These relationships must be understood before the effluent from such a system is to be understood. The importance of the selected parameters of interest in a forested watershed in presented in Section 2.2. The Walker Branch Watershed Project is described in Section 2.3. The Boston Mountain Project is documented in Section 2.4. A nutrient flux project in the Ozarks is described in Section 2.5. The importance of these issues respect to this thesis is detailed in Section 2.6.

## 2.2 Parameters of Interest

Water quality parameters were selected that would best test the Missouri Department of Conservation's best management practice. There are twelve parameters of interest: pH, conductivity, nitrate ($NO_3$), ammonia ($NH_3$), total nitrogen (TN), soluble reactive phosphorous (SRP), total phosphorous (TP), calcium (Ca), magnesium (Mg), potassium (K), total suspended solids (TSS), and total volatile suspended solids (TVSS).

### 2.2.1 pH and Electrical Conductivity

Conductivity and pH are index tests that are useful in either supporting or refuting the results of other tests. In environmental systems, soil and water, pH is a main indicator of the chemicals present. In other words, in certain circumstances if pH is too high or too low then other factors are involved that could lead to the precipitation of the constituent or leaching of the constituent. Conductivity is also used as an index test to validate the amount of calcium and magnesium present; however, conductivity is a measure of cations. If there is a high conductivity but low calcium and magnesium present, then there are other constituents that are adding to conductivity in the sample and should therefore be further explored.

### 2.3 Nutrients

The more important nutrient cycles that occur within forested are described in Table 1. These nutrients are important to the maintenance of the forest ecosystem. Phosphorous, potassium, calcium, and magnesium originate in the parent material. However, nitrogen must be recycled from organic matter or fixated from the atmosphere.

**Table 2.1: Summary of Features of the Major Nutrient Cycles (Fisher, Binkley; 2000)**

| Element | Major Pool Used by Vegetation | Major Long-Term Source for Vegetation Uptake | Biochemical Roles | Limiting Situations |
|---|---|---|---|---|
| **Nitrogen** | Soluble Nitrate, exchangeable ammonium, N2 for nitrogen fixing species | Soil organic matter, atmospheric N2 for nitrogen-fixing species | Proteins, enzymes, nucleic acids | Most Temperate forests |
| **Phosphorous** | Soluble phosphate | Soil organic matter, adsorbed phosphate, mineral phosphate | Nucleic acids, lipids, energy flow | Old soils high in aluminum and iron |
| **Potassium** | Soluble K+ | Soil organic matter, exchange complex, mineral potassium | Enzyme cofactor, membrane, ionic strength buffer | Old soils, if nitrogen and phosphorous is added via fertilizers |
| **Calcium** | Soluble Ca2+ | Soil organic matter, exchange complex, mineral calcium | Cell walls, also present as calcium phosphate and calcium oxalate | Rarely limiting |
| **Magnesium** | Soluble Mg2+ | Soil organic matter, exchange complex, mineral magnesium | Enzyme cofactor in chlorophyll Rarely limiting | Rarely limiting |

**2.3.1 Nitrogen**

Nitrogen exists in many forms: Ammonia ($NH_3$), nitrate ($NO_3$), ammonium ($NH_4$), nitrogen gas ($N_2$), and nitrite ($NO_2$). Ammonium and nitrite are intermediate stages of nitrogen and thus are not readily found in a forested watershed. Nitrogen does not exist in parent material and must come from the atmosphere (fixation) or deposition (decaying organic matter and precipitation events) (Henderson, Johnson; 2002). Nitrate and ammonia are used by plants and microbes as energy sources. Nitrification and denitrification are the two main processes that govern nitrogen changing forms. Nitrification occurs when $NH_3$ is taken in by plants and soil heterotrophs and then converted into nitrate which is used to construct proteins for growth in an oxidative process. Denitrification is the reduction of nitrate to nitrogen gas. If the nitrogen supply is greater than the demands of soil heterotrophs and vegetation, then nitrate leaching into the watershed occurs (Henderson, 2002). The study of nitrogen is important because nitrogen is not only a main contributor to the growth of the forested watershed, but also because nitrogen availability limits growth more than any other nutrient (Binkley, 2000). In regard to silivicultural practice, the canopy of a tree contains one-half of a tree's nitrogen pool (Binkley, 2000). A tree's canopy is often left as slash after tree harvesting is completed. This allows for either rapid regrowth of the deciduous trees or leaching of nitrogen from the brush pile into the watershed will occur (Stone, 1975).

**2.3.2 Soluble Reactive Phosphorous and Total Phosphorous**

Phosphorous is not only an important nutrient for plant growth, but like nitrogen, is limited in many systems. With regard to phosphorous, the Ozark ecosystem includes those with old, weathered soil that have large concentrations of aluminum and iron.

There are three main phosphorous pathways:  Phosphorous can be taken in by plants, precipitates in the presence of calcium, iron, and aluminum, or phosphorous may be leached from the root system (Binkley, Fisher; 2000). These processes are pH dependent (Nien-Tzu, 1997).  Binkley and Fisher reported that soil containing calcium phosphate, were the most soluble and tended to have a higher pH.  Soil containing aluminum phosphate was the least soluble and had the lowest pH.  In the Ozarks, it was found that the phosphorous was distributed with regard to landforms and soil depth.  Most phosphorous was in the A-horizon, and decreased with depth due to high levels of aluminum and iron within the C-horizon (Nien-Tzu, 1997).  The phosphorous in the A-horizon is considered soluble phosphorous obtained through long decomposed organic material (Binkley, Fisher; 2000).  This form of phosphorous can easily be determined by measuring for soluble reactive phosphorus in the watershed's effluent (Binkley, Fisher; 2000).  Timber harvesting was not shown to have great detriment to phosphorous stores as they are retained by geochemical processes.  However, erosion, or mass wasting of soils, was found to be a detriment to soil stores (Binkley, Fisher; 2000).  Nien-Tzu (1997) noted that the Ozarks may become a phosphorous-limited system if soil is not properly managed.

### 2.3.3 Potassium

Like phosphorous, potassium is limited in a system that is dominated by old soil. Potassium is released by decomposition and half the mass of potassium can be located in the forest's litter layer (Binkley, Fisher; 2000).  Potassium is the most mobile nutrient but can be sequestered by clays which then limit its use by plants.  This nutrient not only acts

as a pH buffer but also is used in plants for enzyme activation, protein synthesis, and photosynthesis (Binkley, Fisher; 2000).

### 2.3.4 Calcium and Magnesium

There are several key reasons why the measurement of calcium and magnesium are important. The first is that they are useful in deducing major geological characteristics of the site. The Ozarks have these cations since the major geologic formations are dolomitic limestone comprised of calcium and magnesium. The constituents are also an important relation to hydrological characteristics of the stream itself such as the armoring of the channel and other channel characteristics. Calcium and magnesium serve several limnological uses such as buffering of water and enhancing bacterial and plant growth.

### 2.3.5 Total Suspended Solids and Total Volatile Solids

Kathy Doisy, an ecologist from the University of Missouri-Columbia, directed a study entitled "Assessing Effects of Forest Management Practices on Aquatic Resources" to determine the effect of forest management and the geomorphology of streams on the invertebrate communities within Ozark headwater streams (Doisy, 2000). It was found that timber harvesting not only increases the amount of water that enters perennial streams due to reduced evapotranspiration and increased runoff in ridges but also increases sediment yield after the regrowth of stabilizing vegetation. It was also found that organic sediment would serve to enhance invertebrate biodiversity by adding additional energy stores to the stream system. Non-organic sediment served as a stressor to the invertebrate community by altering the stream geomorphology in perennial and ephemeral streams and water chemistry in perennial streams (reducing temperature,

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changing the sun exposure, altering pH, etc.).  It was found that some of the most detrimental silvicultural practices were the construction of logging roads and skidding trails.  Additional observations such as the Walker Branch Watershed Project (Henderson et al. 1989) have been highlighted in previous forest ecosystem studies.

## 2.4 Walker Branch Study

The Walker Branch Watershed Project (Henderson et al. 1989) is located in the Ridge and Valley province of east Tennessee on the Oak Ridge Reservation.  The project began in 1967 with three objectives:  provide data for unpolluted forested areas, contribute to the knowledge of cycling and loss of chemical elements in natural systems, and to enable the construction of models to better predict societal impacts on natural environments.  The Walker Brach Watershed Project utilizes a watershed level approach to better understand the dynamics of the ecosystem under study.  The watershed level approach is a theoretical ecosystem framework that brings together the chemical and water inputs to the ecosystem with the biological and geochemical cycling of the materials deposited, thus forming an integrated cycle for the whole watershed.  The watershed model in use pertains to many facets of the watershed including:  measuring the hydrologic characteristics of a watershed ranging from subsurface flow, variable source area flow, transport across the plant-soil interface, and outflow, the measuring of the chemical composition of wet and dry deposition above ground and biomass located below ground, and the interaction of flow and the pooling of biomass with regard to underlying geology, topography, soils,  as well as understory and overstory vegetation.

The Walker Branch study area is located on the Oak Ridge Reservation in Anderson County, Tennessee near Oak Ridge National Laboratory.  The two basins

eventually drain into the Tennessee Valley Reservoir. The study area covers 98 hectares and consists of two smaller watersheds – the west catchment and the east catchment. The west catchment covers 38 hectares, and the east catchment includes 59 hectares. The entire study area is bound on the north by Chestnut Ridge. The ridge reaches an elevation of 350 m and slopes downward in a southern direction to an elevation of 265 m at the confluence of the two lesser watersheds.

The study area lies within a humid continental climate zone. The annual mean rainfall is 35 in and the median temperature is 52 degrees F. The climate supports a wet winter and dry spring, followed by a wet summer and a dry autumn. July is not only the wettest month with a mean rainfall of 4.4 in but also the hottest month with an average temperature of 85 degrees F (Curlin and Nelson 1968).

Walker Branch's geology is mainly comprised of a 1200 ft thick sequence of siliceous dolomite that can be broken up into four layers (Henderson et al. 1971). The soils of the study area have developed over the four dolomitic soil layers. Most soils that have developed are Ultisols. Primary soil series include those of the Fullerton and Bodine. Fullerton soils occupy the ridgetops and upper-slope positions while the Bodine soils are found on intermediate and lower slopes (Peters et al. 1970). These series are low in base saturation, are acidic due to weathering, and low in nitrogen and phosphorous. The series are also very permeable and are well drained. The soil, although classified mainly as infertile, does support a diversified vegetation regime. The watersheds can be best described as a mixed hardwood forest that includes various oaks and hickory lower in the landscape and pine located higher in the landscape (Harris 1977).

Water is collected from the effluent of the two watersheds by the use of a weir and/or hand sampling. Water samples were taken at base flow conditions from perennial streams and during storm events at specified time intervals in ephemeral streams as well as perennial streams. Water samples were analyzed for calcium, magnesium, potassium, sodium, sulfur, nitrate, ammonium, and phosphorous. Samples were not filtered prior to analysis and the methods of the American Public Health Association were followed. The water quality data collected and analyzed from 1970 to 1974 in the Walker Branch Study is shown in Figure 2.3.
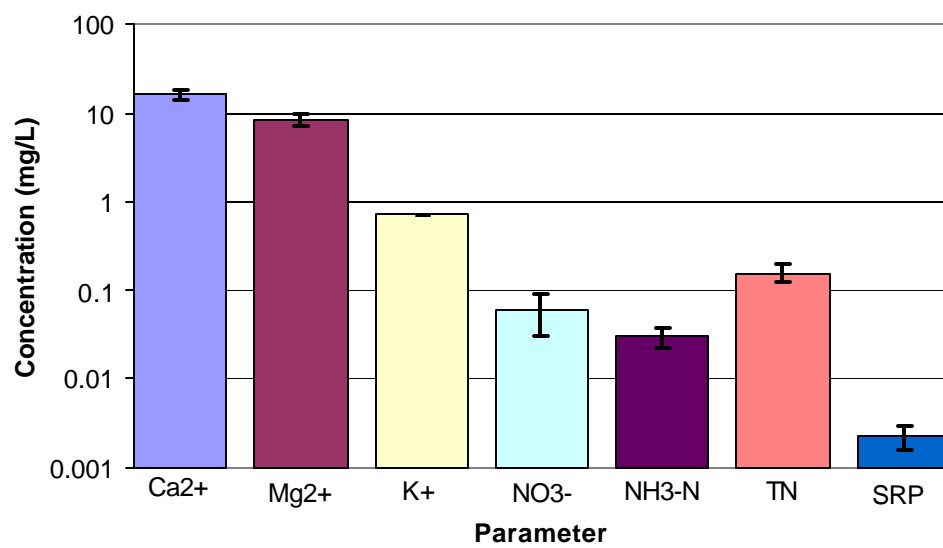
**Figure 2.3: The Average and Range of Various Water Quality Parameters in the Walker Branch Watershed Project for the Years 1970 – 1974**

The Walker Branch Study led to the following observations:

- Nitrate, ammonia-nitrogen, and soluble reactive phosphorous are relatively small and typical of streams draining second-growth forested watersheds in the southeastern United States (Messer et al. 1987).

- The geometric mean of total suspended solids for all samples is 5 mg/L and the mean of pH for all samples is 7.9

- The difference in calcium and magnesium concentration between the two watersheds is due to the proportion of flow emanating from groundwater that has been in contact with the dolomite bedrock. Therefore, it is the time that water is in contact with dolomite (longer residence time) that influences the cations to either be small or large concentrations. The concentrations of the two cations were found to be similar in soils at depth of 75 cm.

- During storms there are three methods that the parameter of interest changes. In Walker Branch, calcium and magnesium show a dilution effect, total nitrogen and soluble reactive phosphorous show a concentration effect. The concentration of potassium varies depending on the season. Potassium levels increase in the watershed's effluent during fall months. The reason for the concentration effect in total nitrogen is due to the leaching of soluble organic nitrogen and the suspension and entrainment of particulate organic materials. Only the largest precipitation events trigger total nitrogen concentration increases.

- Potassium variation is due to the leaching of potassium from fallen leaves and debris from ephemeral channels and intermittent streams in early to late Fall. Soluble reactive phosphorous variation is due to leaching of phosphorous associated with soil

and litter in the upper horizons. The landscape has large amounts of phosphorous in the A-horizon and decreases in the B-horizon (Johnson et al. 1981). Fragipans that inhibit vertical flow, thus increasing lateral flow, could move more water over debris and increase soluble reactive phosphorous in the effluent (Elwood, Turner 1989).

- Nitrate concentration in water samples is highest in the winter and lowest in the summer. This is due to the seasonal pattern in the uptake of nitrogen by vegetation and microorganisms associated with litter and the increase in transport of remineralized nitrogen through the soil due to less evapotranspiration during the late fall-winter period (Elwood, Turner 1989).

## 2.5 Boston Mountain Study

Water quality on stormflow from four forested watersheds located in the Boston Mountains of Arkansas was monitored for eight years (Lawson et al 1985). The samples collected were analyzed for multiple constituents including: potassium, total phosphorous, calcium, iron, sodium, ammonia-nitrogen, magnesium, manganese, nitrate, and carbonic acid. The study site was located in northwest Arkansas on the Ozark National Forest southwest of Fayetteville, Arkansas. The aspects of the four watersheds ranged from west to northeast. The average slope for the watersheds is 30 percent. The watersheds are located on flat bedded sandstone and shales. Soils in the region are derived from sandstone, siltstone and shale of the Atoka formation of the Pennsylvanian Age. Soils vary with regard to landscape position. The soil series range from a fine sandy loam on the ridges and upper slopes to gravelly sandy loams on lower slopes. All soils are infertile, highly acidic, and moderate in permeability. The overstory vegetation

can be classified as mixed hardwoods and consists of white oak, red oak, various

hickories, black oak, and red maple.

During the period 1974 to 1981, stormflow from the four watersheds was

measured using 1 meter flumes in ephemeral streams. One-liter water samples were

collected at various stage heights. Date of storm occurrence was recorded for each

sample. Samples were collected after a storm producing event and stored in a refrigerator

or freezer until analysis could be performed. All laboratory analyses were performed at

the University of Arkansas, using standard methods (American Public Health Association

1980). Analyses were made on unfiltered samples and consisted of the following

parameters: pH, iron, manganese, total phosphorous, potassium, calcium, magnesium,

sodium, total hardness, ammonia nitrogen, nitrate, bicarbonate, specific conductance, and

turbidity.

Water sample data for most nutrients were collected during the entire period

(1974 – 1981). The total number of samples ranged from 159 on watershed three to 243

on watershed one over the study period. Selected water quality parameter data is shown

in Figure 2.4.
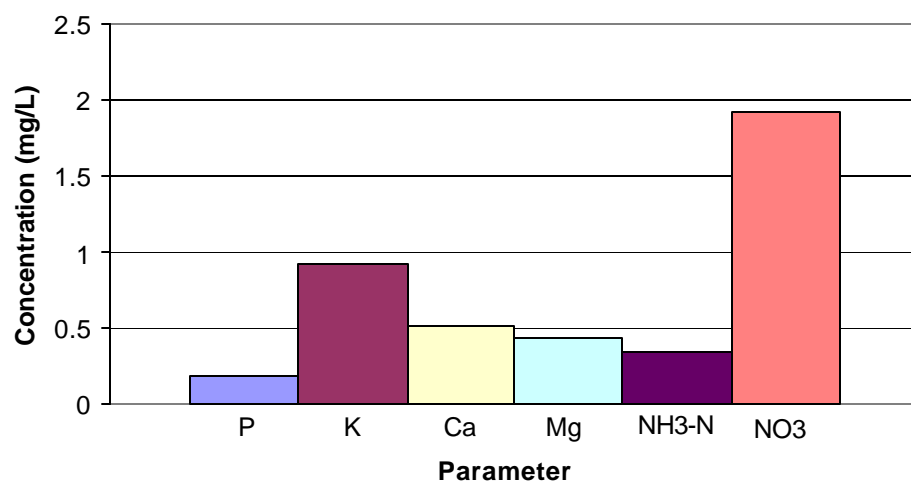
**Figure 2.4: Concentration Mean Summary of Selected Parameters for Watershed Study in the Boston Mountains 1974 – 1981 (after Lawson et al. 1985)**

Multiple observations were made during the eight years of sampling in the Boston Mountain Study, as summarized below.

- Average concentrations of calcium and potassium varied seasonally. In the summer and early fall months, these concentrations increased dramatically. This was explained by increased amounts of these parameters in rainfall events. Thus, seasonal differences in nutrient content in stormflow may be due to varying inputs of nutrients in precipitation.

- Average concentrations of phosphorous and calcium did not differ greatly across the watersheds. Any differences noted were explained by variation in soil and hydrologic response characteristics. Watersheds three and four were found to have less stormflow and higher nutrient concentrations in comparison to watersheds one and two. It is suggested that dilution is the cause for the decreased nutrient levels. Watersheds three and four have greater amounts of soil that are deeper and have thicker surface layers, than watersheds one and two accounted for the difference in hydrologic stormflow response.

- Nitrate was found to be highest in sampling months of July and August.

- Ammonia-nitrate was also found to be the highest in August. Increased nutrient precipitation input is thought to be the reason for the increased concentrations.

- The average pH of stormflow varied among the watersheds. Monthly pH readings ranged from 5.8 in June to 6.3 in January, but did not show any seasonal trends. The pH of precipitation and soil pH levels have been reported to show seasonal trends (Keogh and Maples, 1972). Changes in atmospheric deposition are thought to lower the yearly mean over the eight year study changing the pH

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from 6.1 to 5.6.  Although not a function of timber harvest management, could offer explanation for future trends that could not be blamed on timber harvesting.

- Electrical conductivity levels varied with regard to season and other nutrients. Conductivity was highest in summer and early fall, the same time of the year that coincided with the higher concentrations of most nutrients.  Watershed three has the highest conductivity and also has the highest amount of nutrients.

## 2.6 Missouri Ozark Nutrient Flux Study

As means to better understand the central hardwood area in the Ozark region a streamflow and nutrient flux study was performed by Settergren (1975).  Precipitation inputs and the runoff losses on four watersheds were measured.  The study had two principal objectives: to compare the flux of specific nutrients between the selected sites, and to examine the differences between the concentration of the specific nutrients with regard to the concentrations in streamflow.  The watersheds ranged from 9 – 18 acres and were even-aged predominate hardwood forests.  The sites overlaid carbonate bedrock. The soils were derived from residuum of dolomite and sandstone.  Locally the sandstone was found to be 50 ft thick – Roubidoux layer.  Water samples were collected automatically at each storm event using a large number of single stage samplers.  Grab samples were collected to supplement the data collected in the single stage samplers. Following collection, the samples were frozen until they were analyzed.

Water samples were collected for a two-year period (1973 – 1975).  The flux information is summarized in Tables 2.2 and 2.3.

**Table 2.2: Nutrient Flux for the Year 1973 – 1974 (Settergren et al. 1975)**

| Nutrient Ion | Precipitation 79.52 inches<br>Nutrient Inflow (kg/ha) | Watershed 1 outflow - 24.2 in<br>Outflow (kg/ha) | Watershed 2 outflow - 30.5 in<br>Outflow (kg/ha) |
|---|---|---|---|
| Ca | 7.86 | 10.21 | 107.48 |
| Mg | 1.07 | 5.78 | 73.91 |
| K | 5.17 | 5.51 | 6.41 |
| NH3-N | 9.89 | 3.15 | 1.7 |
| NO3-N | 2.71 | 0.39 | 0.38 |
| TP | 0.68 | 0.25 | 0.06 |

**Table 2.3: Nutrient Flux for the Year 1974 – 1975 (Settergren et al. 1975)**

| Nutrient Ion | Precipitation 52.84 inches<br>Nutrient Inflow (kg/ha) | Watershed 1 outflow - 9.47 in<br>Outflow (kg/ha) | Watershed 2 outflow - 13.45 in<br>Outflow (kg/ha) |
|---|---|---|---|
| Ca | 4.79 | 4 | 44.91 |
| Mg | 0.64 | 2.29 | 29.25 |
| K | 3.09 | 2.22 | 2.9 |
| NH3-N | 5.9 | 1.01 | 0.79 |
| NO3-N | 1.75 | 0.14 | 0.18 |
| TP | 0.38 | 0.05 | 0.05 |

The following observations were made from the data collected in the Ozark Study (Settergren et al. 1975) and are summarized below.

- Watersheds were found to annually lose calcium and magnesium. In wet years, watersheds may lose potassium,

- It was found that the parameters of ammonia-nitrogen, nitrate, and total phosphorous were accumulated,

- Ammonia-nitrogen, phosphorous, potassium, and calcium occur most frequently in early summer and in fall as these nutrients are leached from tree foliage and decomposing leaf litter,

- Concentration of parameters related to storm magnitude and the time since the previous flushing event,

- Potassium and phosphorous yields were closely related to stream turbidity indicating that the parameters were released with flushes of organic and inorganic matter, and

- High yields of magnesium and calcium were associated with winter and spring seasons when increased soil moisture facilitates geologic weathering.

**2.7 Summary**

The water quality parameters selected for evaluation include: pH, electrical conductivity, total suspended solids, total volatile suspended solids, calcium, magnesium, potassium, nitrate, total nitrogen, ammonia-nitrogen, total phosphorous, and soluble reactive phosphorous. These parameters have been selected because of their importance or indicate specific cycling attributes to the forest or their potential to degrade

downstream water stores.  Observations from previous studies can be used to further the understanding of the water samples in the present study.

Three studies were reported as means to explain the results that are gathered in the Missouri Department of Conservation Project.  The Walker Branch Watershed research was fundamental to understanding the processes of a mixed hardwood forest watershed. The study area is in a similar climate regime to the Ozarks and shares similar geologic features.  Samples were collected from perennial streams and from ephemeral streams during storm events.  Water samples collected were analyzed for multiple constituents including:  calcium, magnesium, potassium, nitrate and ammonia-nitrogen, and soluble reactive phosphorous.  The corresponding baseline values for the years of 1970 to 1974 were found to be 16 mg/L, 8.4 mg/L, 0.73 mg/L, 0.03 mg/L, 0.06 mg/L, The effluent from these sites was not the only means of measurement however.  The selected parameters were measured in terms of deposition, plant uptake, and soil retention as well. The research led to conclusions on how multiple variables could affect the effluent of their study areas.  The Walker Branch data may prove pivotal in trying to better understand the concentrations found in samples collected from the Ozarks study area.

The research conducted in the Boston Mountains in Arkansas shares similar importance.  The Boston Mountain study was also focused on ephemeral streams and the concentrations of various parameters in water samples that originated from four watersheds over an eight year period.  The parameters measured included:  total phosphorus with an average concentration of 0.18 mg/L, potassium with an average value of 0.92 mg/L, calcium and magnesium with values of 0.51 and 0.43 mg/L respectively, and ammonia-nitrogen with 0.34 mg/L and nitrate with an average of 1.93 mg/L.  The

study sites were located in the Ozark National Forest and were characterized as mixed hardwood forests. Parameters were analyzed that are similar to those analyzed in the Missouri Department of Conservation Timber Harvest Study.

The streamflow and nutrient flux study was performed in the Ozarks. The study has provided essential information about seasonal trends in the same setting as this Timber Harvest Project for many of the same parameters. In addition to this, the study gives information about the hydrology of sites similar to the Timber Harvest sites. Settergren et al. 1975 indicates yearly precipitation and the amount of effluent that came off of the four watersheds. The data indicates that on average from 20 to 30 percent of the water that falls on the sites leaves the sites as surface flow. There are a multitude of additional forestry projects on the topic of water quality and timber harvesting (Swank et al. 1979, Correll, 1996, Aubertin et al. 1974, Borg et al. 1988, Hupp et al. 1993, Bateridge, 1974, Brown et al. 1973, Cooper et al. 1969, Fredrikson, 1971, Likens et al. 1970, Pierce et al. 1970). However, most of these projects are located in different climatic regimes or are coniferous forests and as such were not selected for review.

**Chapter 3 – Methods and Materials**

**3.1 Introduction**

Fifteen sites were selected for instrumentation. The sites are located in Shannon and Reynolds counties. Eight sites are located in the Angeline Conservation Area and seven sites are located in the Current River Conservation Area. Ten of the fifteen sites will be harvested and the remaining five will serve as controls. The instrumentation installed at the sites was designed to collect water samples during precipitation events that create surface flow on side slopes and within ephemeral drainage ways. A discussion of site locations and characteristics as well as instrumentation can be found in Bunger (2005). The water samples collected to January 31, 2006 were used to establish the background (pre-harvest) water quality parameters to be used in comparison with post-harvest water samples. All water samples collected were analyzed for the following constituents: pH, conductivity, total suspended solids (TSS), total volatile suspended solids (TVSS), calcium (Ca), magnesium (Mg), potassium (K), nitrate ($NO_3$), ammonia ($NH_3$-N), soluble reactive phosphorous (SRP), total phosphorous (TP), and total nitrogen (TN). The data were compiled using Excel®. The quantitative baseline concentration for all species was defined using "the three sigma method" (Duncan, 2002). The "three sigma method" will be used because many parameters within a forested watershed have been shown to vary by $100 - 1000$ fold at a given level of stream flow (Pope, 1977). The parameters selected to be analyzed are listed in Section 3.2. The methods selected for each parameter are described in Section 3.3. Sample parameter preservation is described in Section 3.4. Challenges that arose in laboratory testing are described in Section 3.5.

Further elaboration on "the three sigma technique" (Duncan, 2002) is given in Section 3.6. A summary is provided in Section 3.7.

**3.2 Selection of Water Quality Parameters**

Many water quality parameters could be analyzed with this project as the project exists at a forest/ water interface. A list of possible parameters is shown in Table 3.1.

**Table 3.1: Possible Water Quality Parameters for the Timber Harvest Study**

| pH | Electrical Conductivity | Total Suspended Solids |
|---|---|---|
| Total Volatile Suspended Solids | Total Phosphorous | Soluble Reactive Phosphorous |
| Total Nitrogen | Ammonia | Nitrate |
| Total Organic Carbon | Calcium | Magnesium |
| Potassium | Sulfur | Iron |
| Manganese | Aluminum | Biological Oxygen Demand |

Of the possible parameters listed in Table 3.1, twelve parameters were selected. A list of these parameters is given in Table 3.2.

**Table 3.2: Water Quality Parameters selected for the Timber Harvest Project**

| pH | Electrical Conductivity | Total Suspended Solids |
|---|---|---|
| Total Volatile Suspended Solids | Total Phosphorous | Soluble Reactive Phosphorous |
| Total Nitrogen | Ammonia | Nitrate |
| Calcium | Magnesium | Potassium |

Aluminum and iron were analyzed on 30 samples. This was conducted because the samples were stained upon field collection and it was hypothesized that these metals, through chelating, could have been the cause. The results can be found in Appendix 14. The significance for the selected parameters is described in Chapter 2, Section 3.

**3.3 Selection of Test Methods for Water Quality Parameters**

The water quality parameter testing methods were based upon the criteria shown in Table

3.3. The testing methods for each parameter of interest are given in Table 3.4

**Table 3.3: Test Method Selection Criteria**

- Applicable/Effective over a wide range of concentrations,

- Method detection limit = 0.01 mg/L,

- Acceptable production rate (Analyze large number of samples quickly),

- The methods had to be verifiable, and

- The methods had to be relatively easy to use.

**Table 3.4: Method Detection Limits and References for the Methodologies Used to Analyze Water Quality Parameters**

| Parameter | Symbol | Detection Limit | Procedure |
|---|---|---|---|
| pH | | Range 2.00 – 13.00 | Probe-Oakton pHtestr[1] |
| Electrical Conductivity | (EC) | 0.01 us | Probe-Corning441[2] |
| Total suspended solids | (TSS) | 0.001 g/L | APHA[3] 2540 D |
| Volatile solids | (TVSS) | 0.001 g/L | APHA 2540 E |
| Total Nitrogen | (TN) | 0.01 mg/L | APHA 4500-NO3 E |
| Nitrate | (NO$_3$) | 0.01 mg/L | APHA 4500-P.E |
| Ammonia-N | (NH$_3$-N) | 0.01 mg/L | MCWW[3] 351.2 |
| Total Phosphorous | (TP) | 0.01 mg/L | APHA 4500-P. E |
| Soluble Reactive Phosphorous | (SRP) | 0.01 mg/L | APHA 4500-P.E |
| Calcium | (Ca$^{2+}$) | 0.01 mg/L | APHA 303 A |
| Magnesium | (Mg$^{2+}$) | 0.01 mg/L | APHA 303 A |
| Potassium | (K+) | 0.01 mg/L | APHA 303 A |

1. A pH probe located in Lafferre Hall at the Soil Characterization Lab

2. A conductivity probe located in Lafferre Hall at the Soil Characterization Lab

3. American Public Health Association

4. Methods for Chemical Analysis of Water and Wastes

The procedural steps and approximated times required to analyze all constituents are shown in a flowchart (Figure 3.1). The flowchart begins with incoming water samples that have been placed in a freezer at -10°C. Sample separation is the first step. This step includes the testing of pH and electrical conductivity, the recording of the sample's volume, and isolating a portion of the sample in a 60 ml bottle for future analyses. The second step is dissolved separation in which 100 milliliters of the sample are filtered through a 0.45 um glass fiber filter. The filter is retained for solids analysis and the filtrate is retained for dissolved analysis. The dissolved nutrients in the samples can then be analyzed using the methods listed in Table 3.1. A digestion step is required to breakdown the suspended matter of the samples so that the various unanalyzable nutrient forms can be released and analyzed. After this digestion step, the solution can then be analyzed for total nitrogen and total phosphorous.
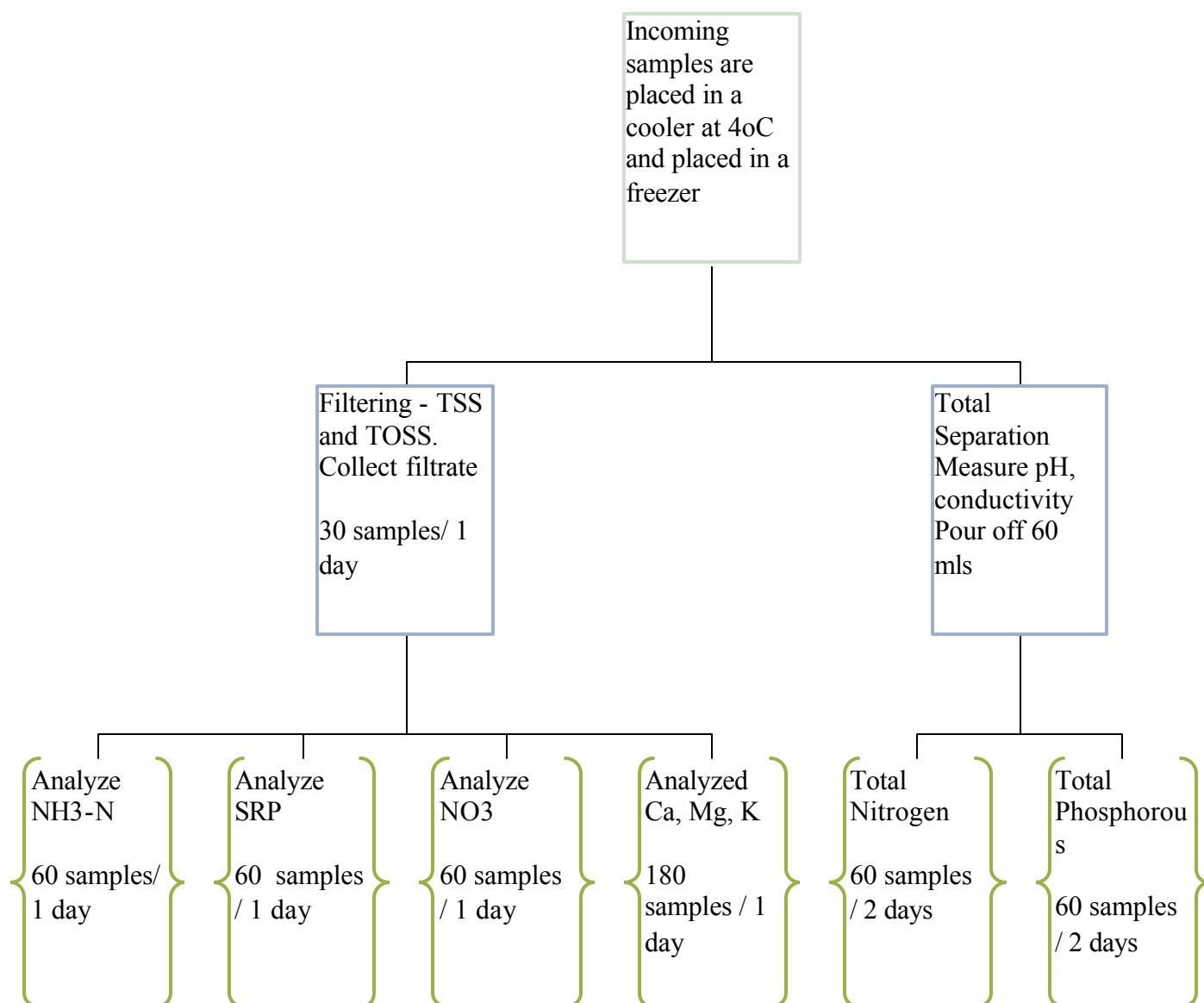
**Figure 3.1: Flow Diagram Depicting Lab Activities and Associated Durations**

**3.3.1 Total Suspended Solids and Total Volatile Suspended Solids**

Total suspended solids and volatile suspended solids were analyzed by using APHA Standard Methods (APHA, 1998). Total suspended solids were analyzed by pouring one-hundred milliliters of sample through a 0.45 um clean glass fiber filter. The filter was dried at $105^{o}C$ for 24 hours and weighed. The scale had to possess the capacity to read 0.0001 g. Deionized water was used to wash the filtering apparatus after every sample. A blank filter sample was used every five samples. The standard operating procedures (SOP) for TSS is located in Appendix 2. Volatile suspended solids were analyzed by placing the filter into an oven at $550^{o}C$ for 24 hours and then re-weighing the filter thus ridding the filter of all organics. The SOP for total volatile suspended solids is located in Appendix 3.

**3.3.2 Total Phosphorous and Soluble Reactive Phosphorous**

Total phosphorous and soluble reactive phosphorous share the same examination technique but have different sample preparations. The first stage for Total Phosphorous (TP) is digestion that utilized potassium persulfate digestion (APHA, 1998). Soluble reactive phosphorous did not require any steps before analysis. The Ascorbic Acid technique; APHA Method 4500 P.E (APHA, 1998) was used to analyze both parameters. The samples were analyzed on a Spectron 20D+ spectrophotometer housed in the Soil Characterization Laboratory (SCL) in Lafferre Hall. Total phosphorous and SRP was quality controlled by the use of standards and blanks. A quality control digestion standard was not needed for total phosphorous (Solorzano, 1980). An SOP for the Ascorbic Method is located in Appendix 4. An overview of the Ascrobic Acid method was detailed in Section 3.3.2.1

**3.3.2.1 Ascorbic Acid Method Overview**

Ammonium molybdate and potassium antimonyl tartrate react with orthophosphate in an acidic state and is then reduced by ascorbic acid to turn the sample's color to blue if orthophosphate is present. The degree to which this blue color is formed is read by the Spectron 20D+ at a wavelength of 660 nm or 880 nm. A summary of the potassium persulfate digestion technique is described in Section 3.3.2.2.

**3.3.2.2 Potassium Persulfate Digestion Overview**

Potassium persulfate digestion, method APHA Method 4500-N C, is required for digestion of total phosphorous and total nitrogen. The samples are digested together as outlined by Ebina, Tsutsui, and Shirai (1983). This technique of digestion oxidizes all nitrogenous compounds to nitrate at $100^{o}C$. The method is important for phosphorous because phosphorous may occur in combination with organic matter; and, digestion releases the phosphorous in its orthophosphate form. A 10 ml sample is mixed with 2.2 ml of persulfate digestion mixture. The mixture was placed in an autoclave for 30 minutes at 98 – 137 kPa.

**3.3.3 Total Nitrogen and Nitrate**

Total nitrogen was digested via the potassium persulfate digestion technique and measured using the cadmium reduction method (APHA, 1998). Nitrate was also analyzed via the cadmium reduction method. As with total phosphorous, the samples were analyzed on the Spectron 20D+ located in the SCL. Chemical pillows, manufactured by Hach, that contain a set amount of chemical per sample amount were used according to Hach Method 8192 (Hach, 2004). The use of chemical pillows rather than cadmium column is preferred because the cadmium column requires 75 ml of

sample and its efficiency of turning nitrate to nitrite decreases with the amount of sample that pours through the column. The cadmium reduction method is outlined in Section 3.3.3.1.

**3.3.3.1 An Overview of the Cadmium Reduction Method**

Nitrate was reduced to nitrite by a copper-cadmium reduction column. The nitrite reacts with sulfanilamide in an acidic medium and forms a diazo compound which couples with N-1 napthylethylendiamine dihydrochloride (NED) to form a reddish color. The solution is then colorimetrically measured at 543 nm.

**3.3.4 Ammonia**

The salicylate method (APHA, 1988; HACH, 2004) was employed to analyze ammonia. As with the Nitrate and TN, pillows manufactured by Hach were used along with Hach's Method 8155. Samples were analyzed on the Spectron 20D+ at a wavelength of 655nm. The SOP for the salicylate method is located in Appendix 1. An overview of the Ammonia Salicylate method is in Section 3.3.4.1.

**3.3.4.1 Ammonia Salicylate Method Overview**

In solution, ammonia combines with chlorine to form monochloramine which then reacts with salicylate to form 5-amoinosalicylate. This chemical is oxidized by sodium nitroprusside to form a blue color which is masked by the yellow color of excess reagent to form a green color which is then analyzed colorimetrically by the Spectron 20D+.

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### 3.3.5 Calcium, Magnesium, and Potassium

Two methods were used to run the samples. Initially, the samples were analyzed using the AA-Spectroscopy methods (APHA, 1998), on a Perkin-Elmer Model 1100 AA Spectrophotometer located in the Soil Characterization Lab. The sample was combusted in an oxyacetylene flame. The machine either reads the concentration via emission of the constituent in the flame, or by the absorption of energy of the sample by a special lamp. The AA-Spectrophotometer broke down, and the remaining analyses were performed on an ICP (Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)). The ICP is a powerful technique for multi-element analysis. In a single scan in the semi-quantitative mode the analyst is able to acquire estimates on practically every element in the periodic table. In the quantitative mode, accuracy and precision is comparable to existing techniques for every calibrated element. In one instrument, the ICP-MS combines the fast throughput capability of the ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy). Quality control is ensured by the use of standards and blanks.

### 3.4 Sample Preservation

Sample preservation methods must take into account field collection time and lab holding time necessary to perform the analyses for all constituents of interest. Sampling occurs when a precipitation event produces enough surface flow to allow capture in the hillslope samplers or in-stream samplers. Samples are stored at $4^{\circ}C$ after they are collected from the field. Upon arrival in the lab, the samples will be frozen at $-10^{\circ}C$. This temperature has been shown to preserve the constituents of interest for eight years with degradation less than 3% (Avanzino, 1993).

Sample collection times, are a pivotal issue in preserving the integrity of the sample constituents. As a result a sample degradation study was conducted to document the degradation of phosphorous (P), nitrate ($NO_3$), and ammonia ($NH_3$) in water samples. Two solutions containing known amounts of P, $NO_3$, and $NH_3$ were added to two plastic bottles identical to those used in the field. These two solutions are labeled "high" and "low" after their relative amounts of constituents. The "high" water sample contained the following amounts: 0.326 mg/L P, 1mg/L $NO_3$, and 1 mg/L$NH_3$. The "low" solution contained: 0.03 mg/L (P), 0.1 mg/L ($NO_3$), and 0.1 mg/L ($NH_3$). Samples of the prepared solutions were analyzed the first day to determine the initial concentrations present in the samples. Sub-samples were then taken from the solutions for four subsequent days under storage conditions that were similar to field conditions. The temperature ranged from $19^{o}C$ at night to $33^{o}C$ in the daytime. The variation of constituents with time can be viewed in the Appendix. In the "high" sample for the four days of testing, phosphorous ranged from 0.32 mg/L to 0.34 mg/L, or suffered no degradation: whereas, $NH_3$-N ranged from 1 mg/L on the first day of the study to undetectable concentrations by the fourth day. Similarly, $NO_3$ ranged from 1 mg/L on the first day of the study to 0.4 mg/L on the last day of the study. The "low" sample had similar trends. Phosphorous ranged from 0.03 mg/L on the first day of the study to 0.01 mg/L on the last day of the study. Both components of nitrogen, however, degraded more extensively. Ammonia degraded from 0.1 mg/L to concentrations below 0.01 mg/L by the fourth day. Nitrate degraded from 0.1 mg/L on the first day to a concentration below 0.02 mg/L on Day 2, before rebounding to a concentration of 0.04 mg/L. These trends are in Figure 3.2.
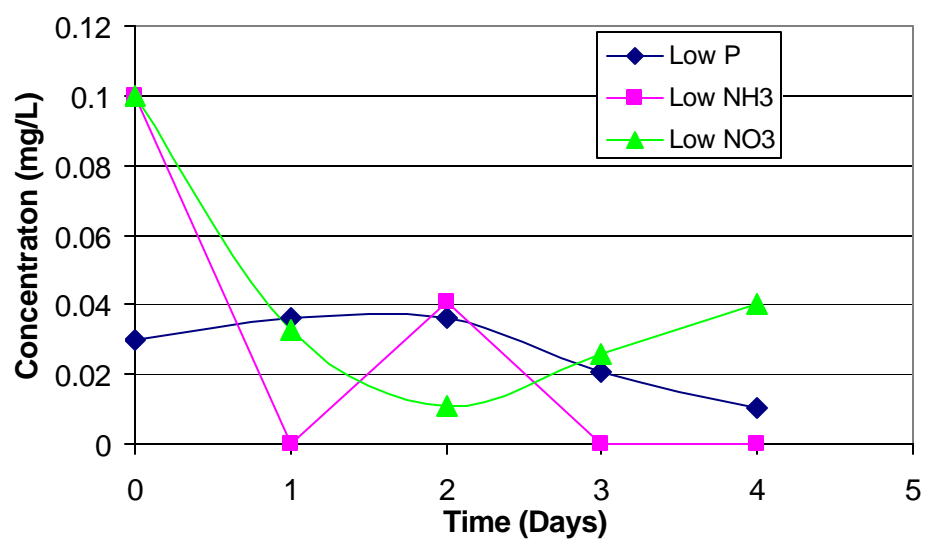
**Figure 3.2: Nutrient Concentrations versus Storage Time in Dictating the Degradation Rate for Nutrients Sampled from the Low Concentration Samples**

These results raise doubts about the reliability of testing $NO_3$ and $NH_3$-N. The only solution to this dilemma is by finding a threshold event that creates flow and then collecting the samples quickly. However, most samples collected contain analyzable concentrations of phosphorous, ammonia-nitrogen, and nitrate. Additional sampling issues have caused difficulty in laboratory testing.

**3.4 Problems in Laboratory Testing**

Staining of collected water samples (Figure 3.2) forced the use of two machines to analyze for $NO_3$, $NH_3$-N, TN, SRP, and TP. The first machine was the AA-Technicon located at the Columbia Environmental Research Center (CERC), and the second device, the Spectron 20D+ located at the Soil Characterization Lab.
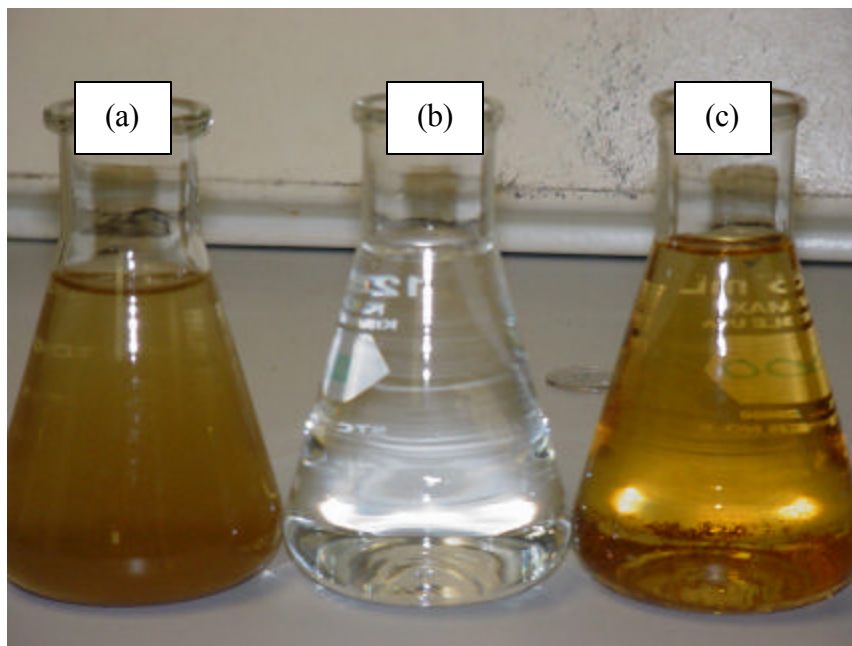
**Figure 3.3:  Staining differences among sampled water.  (a) is from a hillslope samplers (b) is from an in-stream sampler (c) is from an in-stream sampler**

The staining interferes with the analysis methods for these constituents. The changes in color coupled by the staining of the samples results in exaggerated readings by deepening the hue of the detected color, thus decreasing the detection limits. The AA-Technicon was unable to account for the sample stain because it could not analyze the untreated sample and reagent added sample together. The Spectron 20D+, a manual spectrophotometer, can take staining into account. The stained, untreated sample can be analyzed at the appropriate wavelength. And then the sample can be treated with the reagents and then re-analyzed. The actual concentration is the difference between these readings.

A study was conducted to compare results between the Spectron 20D+ and the AA-Technicon. The study was designed to test the precision and accuracy of the Spectron 20D+ on the three methods used for analysis – Cadmium Reduction method, Salicylate method, and Ascorbic Acid method. Twenty-two samples previously analyzed on the AA-Technicon where re-analyzed on the Spectron 20D+. The samples had concentrations ranging from 0.01 mg/L to greater than 1 mg/L. The full results of the study can be located in the Appendices B through D. All but three samples in the Salicylate Method comparison test ($NH_3$ analysis) yielded the same concentrations attained by the AA-Technicon. These three samples had the following percentage of correspondence: 86%, 88%, and 96%. The Cadmium Reduction Method (analysis for $NO_3$ and TN) had similar results. There were five samples that did not have perfect agreement. Of those five, only one sample was below 98% agreement. The Ascorbic Acid method had the greatest differences in concentrations. Of the 22 samples tested, 14 samples were in agreement. These samples deviated by an average of six percent. This

is because the detection limit of the AA-Technicon is 3.2 ug/L and the detection limits of the Spectron 20D+ is 12 ug/L. Based upon the data; the two machines are in agreement.

**3.6 Quantification of Background Levels for Water Quality Parameters**

Numerous factors act independently or simultaneously which result in variation in the water quality parameters. Factors can include: time of season, frequency and duration of precipitation event, aspect of site, geology, vegetation type and density, among many other things. This would mean difficulty in establishing background levels for the constituents of interest. The large variations in concentrations for a given parameter make it difficult to establish a background level. For example, total suspended solids range from 0 g/L to 1.12 g/L.

Quantifying the baseline amounts of all parameters could be accomplished by the "The three sigma method" (Duncan, 2002). Table 3.5 is the steps to use the "the three sigma method"(Duncan, 2002). And Figure 3.4 is a schematic of the three sigma method (Duncan, 2002).

**Table 3.5: Steps for the "Three Sigma Method"**

- Construct a histogram using the data collected

- Fit this data with a distribution (Normal or Lognormal). This distribution would inherently adopt certain characteristic parameters like the mean, the average of all samples, and the standard deviation, or measure of the variation of parameter concentrations

- Establish a cut-off at three times the standard deviation added to the mean $(3s + \mu)$

- The concentrations bounded by the area under the curve formed by the distribution would account for 99.87% of total values. Thirteen samples out of 10,000 samples would exceed this established boundary.
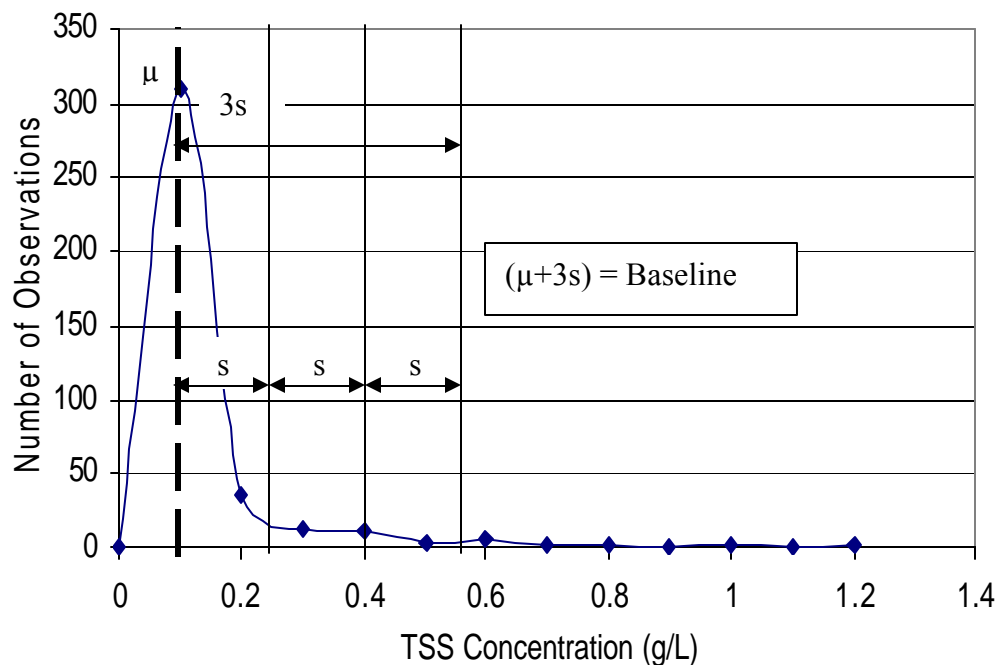


**Figure 3.4: Schematic of Three Sigma Method for TSS (Duncan, 2002)**

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The three sigma method is used to establish background (pre-harvest) for TSS as an example (Figure 3.4). The distribution pictured in Figure 3.4 is a compilation of TSS data concentrations for all samples collected from October 2004 through January 31, 2006. The distribution is based upon 384 samples with a mean of 0.08 g/L and a standard deviation of 0.14 g/L. The "three sigma rule" was used and a background (pre-harvest) concentration of 0.50 g/L is established for TSS in low order ephemeral streams in the Missouri Ozarks.
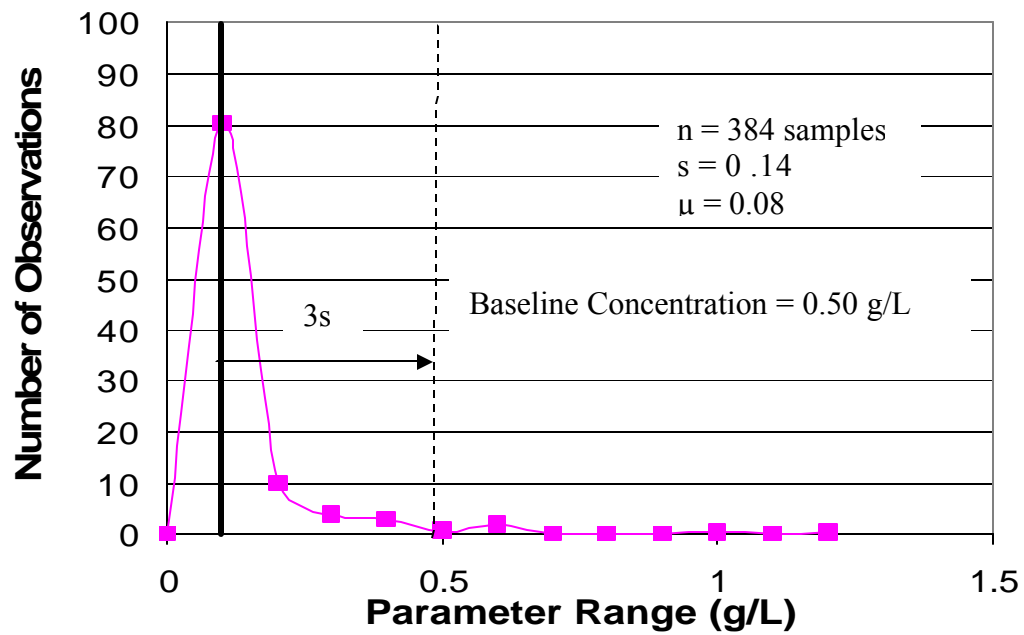
**Figure 3.5: The Three Sigma Rule to Establish Background Level for Total Suspended Solids (TSS)**

**3.6 Summary**

1. Parameters were selected that are appropriate for the statutes of the project

2. Methods have been established that meet all the criteria. They have proven to work well on both machines selected for analysis. Preservation methods have been selected that enable samples to be detained for several years if needed.

3. Sample research has shown that degradation of nitrate and ammonia occur within a day of retention in the sampling apparatus, and that phosphorous does not readily degrade. Sample collection must commence immediately after a precipitation event that has triggered overland flow.

4. The Three Sigma method was used as means to quantitatively set a background (pre-harvest) level for all parameters.

**Chapter 4 - Results and Discussion**

**4.1 Introduction**

Pre-harvest sampling began in October 2004. Pre-harvest data through January 31, 2006 are incorporated in this thesis. Three hundred and eighty four samples were collected in this timeframe. These samples originated from all fifteen sites and from both the in-stream samplers and hillslope samplers. The parameters of interest were analyzed for spatial and temporal variation as means to better understand nutrient cycles within the sites for the parameters of interest, and to understand processes in ephemeral drainage ways. The origination of the collected water samples is presented in Section 4.2. A summary of all results is presented in Section 4.3. Section 4.4 details parameters that vary with season. A summary of the collected data and main points on the variations of parameters is presented in Section 4.6.

**4.2 Collected Water Sample Origins**

Sample collection has been an ongoing process for over a year. Within this time frame there have been 12 sampling trips. The cumulative precipitation records as well as the total number of samples collected are documented in Figure 4.1(a). More rain precipitation events occurred in the first fall of the study to winter 2005 than occurred in the late spring and the fall sampling events in 2005. The types and amounts of samples collected is in Figure 4.1(b)
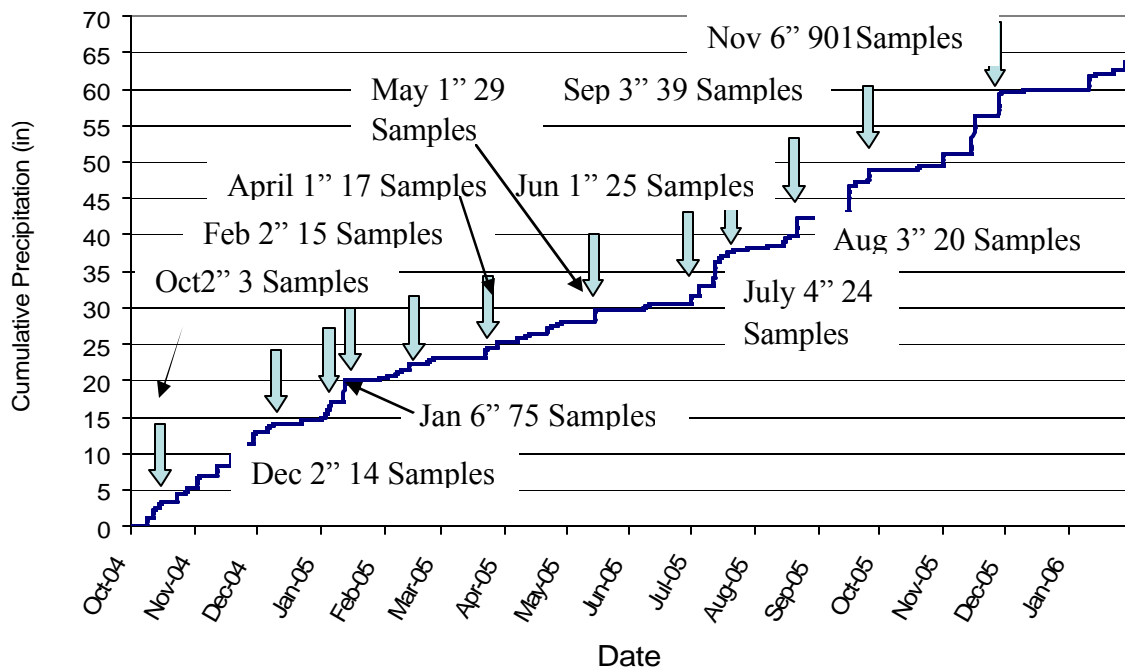
**Figure 4.1(a): Cumulative Monthly Precipitation and Amount of Samples Collected**
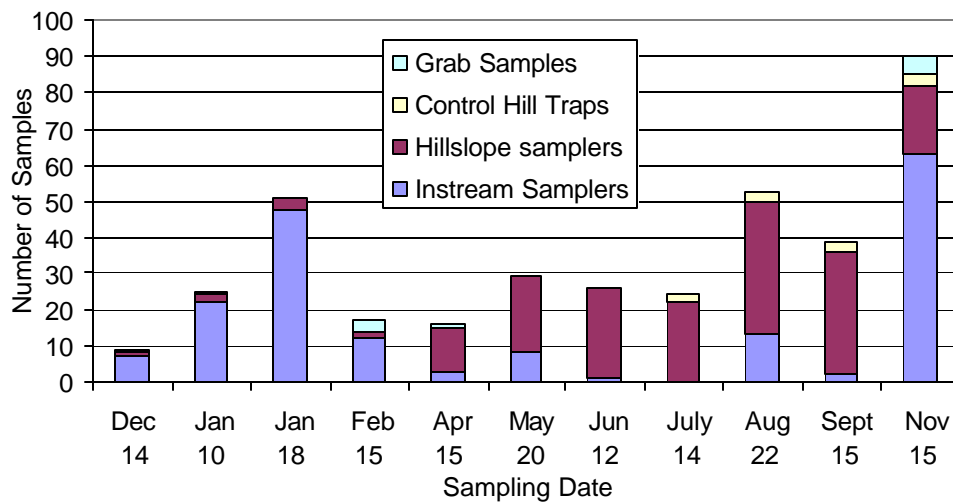


**Figure 4.1(b) Origin of Water Samples Collected Versus Sampling Date from December 2004 to November 2005**

The numbers of samples are related to not only the cumulative precipitation event but more directly to the precipitation event. January 2005 had two sampling events (January 19, 2005 and January 18, 2005). Six inches of cumulative precipitation resulted in 75 samples being collected. The origin of those samples is shown in Figure 4.1(b). The sample trips were initiated by two 2.5 inch precipitation events. The February sampling trip resulted from a 1 inch rainfall in a 24 hour period. Twelve in-stream samples, a grab sample, and two hillslope samples were collected. The April sampling event was also triggered by an inch of rain over a 24 hour time period. Twelve hillslope samples were collected, three in-stream samplers were collected and a grab sample was also collected. Hillslope sampler numbers increased after April of 2005 due to hillslope samplers retrofits. The retrofits included the addition of two ft wide plastic sheeting that was intended to seal up the junction of the gutter to the forest floor. The retrofits were not totally completed until the May sampling date. An inch rainfall event over a half a day triggered the May sampling event. In all, eight in-stream samples and 21 hillslope sampler samples were collected. The June sample collection trip was the result of 0.5 inch to 1.5 inches of rainfall from 6/12/05 to 6/16/05. One in-stream sample and 25 hillslope sampler samples were collected. Decreasing in-stream samples could be attributed to a lack of antecedent soil moisture. This can be verified in Figure 4.1a. Three inches of precipitation over a 24-hour period initiated a collection trip in July. Twenty-two hillslope sampler samples as well as two hillslope samplers control samples were collected. The hillslope control samples were installed to check the efficiency of the hillslope sampler retrofits. Control hillslope samplers continually collected samples after installation. The August sampling trip was triggered by a cumulative 3.5 inch

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precipitation event over seven days. Thirteen in-stream, 37 hillslope samplers, and 3 control hillslope sampler samples were collected. A three inch precipitation event over a thirty-six hour time period triggered the September sample collection. Two in-stream, 34 hillslope and, three hillslope control trap samples were collected. A total of 5 inches of rainfall over a 28 hour period triggered the November sampling date. The heaviest rainfall was 2.5 inches over a three hour period. Ninety-one samples were collected even though sites CR11-1, A27-1, and A27-2 were not visited due to safety concerns. Grab samples were collected on the December 2004 trip, the first January 2005 trip, the February 2005 trip, April 2005 trip and the November 2005 trip. The presence of water in the ephemeral channel upon collection indicates high amounts of antecedent moisture and/or a high intensity precipitation event. The times of collection mirror the climatic conditions discussed in Section 2.3. No in-stream bottle samples were collected on the July sampling trip even though a three inch precipitation event occurred: A result of low antecedent moisture that can be observed in Figure 4.1(a) that also is similar to documented climatic seasonal trends. However, the August event did yield in-stream samples. Wet Augusts are often experienced in the Ozarks. The type and the amount of samples collected for each study site are shown in Figure 4.2.
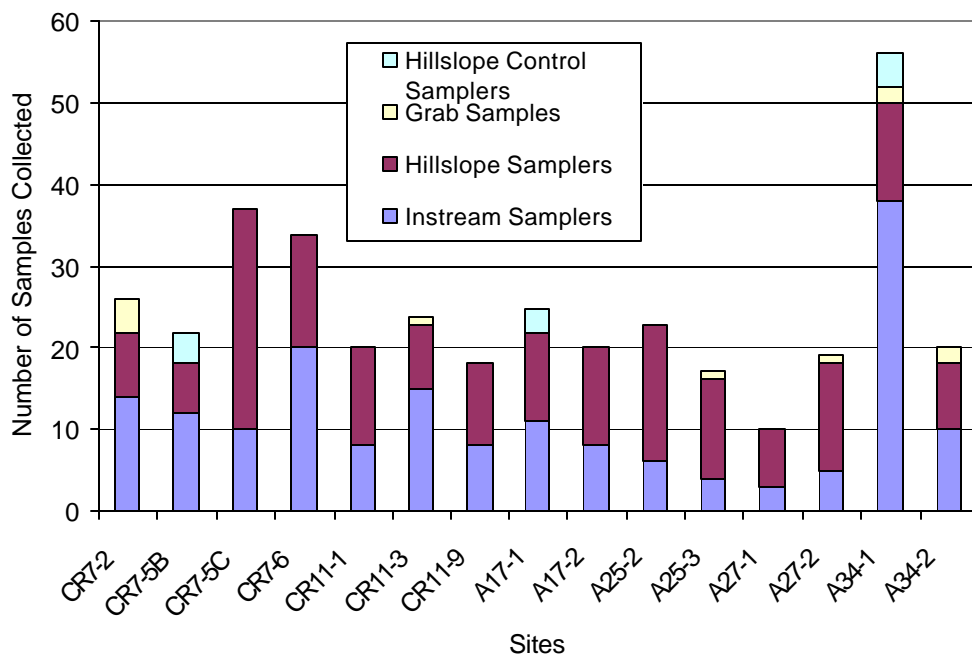
**Figure 4.2 Samples Collected Organized by Site and Method of Collection: From October 2004 to January 2006**

Specific site characteristics regarding geology, basin area, bifurcation ratio, average slope, and others dictate the amount of water samples collected. Bifurcation ratio is the ratio of tributary streams (ephemeral streams) that feed into the main channel. Site A27-1 collected the least samples with 10 and A34-1 collected the most with 56 samples. Site A34-1 has 16 total instruments installed, whereas, A27-1 has only13 instruments. Current River sites collected between 18 and 37 samples. Angeline sites collected between 10 and 56 samples. Current River sites were not only instrumented first, but were the first sites that underwent hillslope sampler retrofits. Sites CR7-6 and site A34-1 produced the most in-stream water samples. This is due to a myriad of site variables that differ from site to site. These variables are better highlighted in an unpublished work by Mueller that is due out in 2006. Although samples were collected during all precipitation events, due to problems with storage and parameter additions, parameters were not analyzed for collected water samples.

**4.3 Summary of Results**

The results for all 12 parameters are summarized in Table 4.1. The results in Table 4.1 are a composite of the in-stream and the hillslope samplers. There exists large variation among the twelve parameters.

**Table 4.1 Summary of All Water Quality Data Collected from both In-stream and Hillslope Instruments**

| Parameter | Number of Samples Collected | Average | Standard Deviation | Max | Min |
|---|---|---|---|---|---|
| pH | 334 | 6.19 | 0.72 | 9.49 | 4.90 |
| Conductivity (us/cm) | 334 | 45.33 | 51.43 | 432.00 | 4.16 |
| TSS (g/L) | 384 | 0.08 | 0.14 | 1.14 | 0.00 |
| TOSS (g/L) | 233 | 0.03 | 0.05 | 0.36 | 0.00 |
| Ca (mg/L) | 334 | 3.62 | 3.13 | 19.65 | 0.04 |
| Mg (mg/L) | 334 | 1.60 | 2.81 | 28.00 | 0.01 |
| K (mg/L) | 334 | 2.27 | 2.70 | 18.10 | 0.00 |
| TP (mg/L) | 334 | 0.28 | 0.36 | 3.35 | 0.00 |
| SRP (mg/L) | 334 | 0.17 | 0.29 | 1.99 | 0.00 |
| $NH_3$-N(mg/L) | 334 | 0.22 | 0.48 | 3.59 | 0.00 |
| $NO_3$ (mg/L) | 334 | 0.16 | 0.39 | 3.70 | 0.00 |
| TN (mg/L) | 334 | 1.43 | 1.45 | 10.04 | 0.01 |

Total suspended solid is the only parameter that was analyzed for all 384 water samples. The samples from, June 2005 and July 2005, were not properly stored. Due to this, most parameters were analyzed on 334 samples not 384. Total Organic Suspended Solids were analyzed for only 233 samples beginning in June of 2005. This is because it was not decided that this parameter would be of interest until that time.

The parameters that were analyzed showed great variability and begin to indicate the importance of the landscape on the effluent collected. The parameter, pH, had an average of 6.19 a max of 9.49 and a minimum value of 4.9. This value fits within the ranges that were discussed in the literature review. However, the range is greater than recorded in either study. pH ranges from 5.8 on site A17-1 to 7.16 on site CR7-2. Angeline Sites have an average pH of 6.28 and the Current River sites have an average pH of 6.43.

Electrical conductivity has an average value of 45.33 us/cm a maximum value of 432 us/cm and a minimum value of 4.16 us/cm. This value exceeds the value documented in the Boston Mountain study (Lawson et al, 1985). However, the underlying geology was different from the study areas in the Ozarks. The conductivity is related to the amount of calcium and magnesium present. Calcium had an average concentration of 3.62 mg/L, a maximum value of 19.65 mg/L, and a minimum concentration of 0.04 mg/L. Magnesium had an average of 1.62 mg/L, a maximum concentration of 28 mg/L and a minimum of 0.01 mg/L. The average of these values is less than the averages reported by the Walker Branch study (Henderson et al 1989). However, the samples collected from the Walker Branch study mainly consisted of samples from perennial streams that would have a greater amount of underground water

which contains higher amounts of calcium and magnesium due to longer residence times in the thick interwoven formations of dolomite. The Ozark study is primarily focused on surface flow and as such the water is expected to have less calcium and magnesium present than subsurface flow.

Total suspended solids and total organic solids were similar in distribution. Total suspended solids had an average concentration of 0.08 g/L and total organic suspended solids had an average value of 0.03 g/L. The maximum concentration for TSS was 1.14 g/L, whereas, the maximum value for TVSS was 0.36 g/L. Total suspended solids and total organic suspended solid data obtained far exceed the values documented in the Walker Branch study (Henderson et al. 1989) and the Boston Mountain study (Lawson et al. 1985) cited in Sections 2.4 and 2.5. Total suspended solids and total organic solids were found not to vary with instrument type.

Phosphorous and nitrogen are two compounds that also showed variability. Total phosphorous had an average concentration of 0.28 mg/L, a maximum concentration of 3.35 mg/L, and the minimum value was below the detection limit. Similarly, soluble reactive phosphorous had a slightly lower average concentration of 0.17 mg/L, a maximum concentration of 1.99 mg/L and a minimum concentration less than the detection limit. The concentrations recorded in water samples from the present study are greater than recorded by either the Walker Branch or the Boston Mountain study. There was no consistent variation with regard to sampling apparatus.

Nitrogen and its components are important with water quality parameters that showed large variations. Total nitrogen had an average of 1.43 mg/L, a maximum concentration of 10.04 mg/L, and a minimum concentration of 0.01 mg/L. These

recorded concentrations far exceed the average concentration documented by the Walker Branch study (Henderson et al. 1989) (nitrogen concentration of 0.16 mg/L). Ammonia-nitrogen and nitrate are components of nitrogen that were also analyzed. Ammonia-nitrogen had an average concentration of 0.22 mg/L and a maximum value of 3.59 mg/L whereas nitrate had an average concentration of 0.16 mg/L and a maximum value of 3.7 mg/L. Both constituents had a minimum value less than the detection limit. The Boston Mountain study (Lawson et al. 1985) documented that nitrate had an average of 1.92 mg/L and a peak of 3.2 mg/L.

**4.4 Parameters that Vary with Season**

The concentrations of all solutes in water samples collected exhibit seasonal patterns reflecting hydrological and biological processes in the watershed. It must be noted that the data discussed is from samples collected over a period of one year – representing a full cycle of climatic seasons in the Ozark highlands of southern Missouri. The following sections detail seasonal variations in selected parameters.

**4.4.1 Seasonal Variation of pH, Electrical Conductivity, Calcium and Magnesium**

pH and Electrical conductivity follow the same overall trend. An increase is experienced in the winter and decreases in the summer months (Figure 4.3). Previous studies indicate that conductivity was greatest in the summer months due to longer residence times in dolomite rock (Henderson et al. 1989). However, the nutrient study in the Ozarks found a similar pattern with regard to the Ozark Timber Harvest Study (Settergren et al. 1975). Average pH values in the Ozark study ranges from 6.0 in the August 2005 sampling event to 7.2 in the December 2004 sampling event. Whereas conductivity has its highest concentration in the May 2005 sampling event with 114 us/cm and it lowest in the September 2005 sampling event with a little over 20 us/cm. This pH is lower than reported at Walker Branch (pH = 7.9) from 1970 to 1974, but higher than the pH values reported at the Boston Mountain performed from 1974 to 1981 study (pH = 5.8 – 6.3). The geology of the Ozark region supports higher amounts of dolomite thus equating to higher pH. The reason for the higher amount of electrical conductivity and pH is the higher amount of rainfall that occurred in the winter months that is exhibited in Figure 4.1(b).
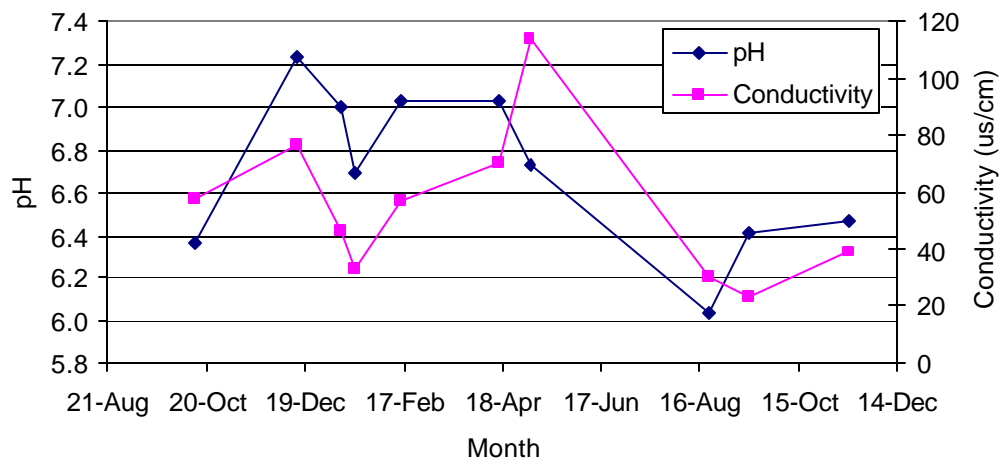
**Figure 4.3 Trends of pH and Conductivity with one Year of Sampling:  for samples collected in October 2004 to Samples collected in November 2005**

Figure 4.3 does not indicate two sampling events - June 205 and July 2005. Seven of the sampling events resulted in the in-stream samplers having a higher pH value than the hillslope samplers. Hillslope samplers contain detritus that when leached could lower the pH of the sample – forming humic acid. Henderson. 1989 shared a similar observation. The second January event and the February 2005 event were the two events that the water samples collected from the hillslope pH was greater than the in-stream pH. This could have been attributed to a higher degree of water being flushed from the site due to high antecedent precipitation that exceeded the dissolution of calcium and magnesium and due to the two sampling events being in winter months that result in a smaller amount of degradation of organic matter. The seasonal trend of calcium and magnesium for samples collected from in-stream samplers and hillslope samplers are shown in Figure 4.4
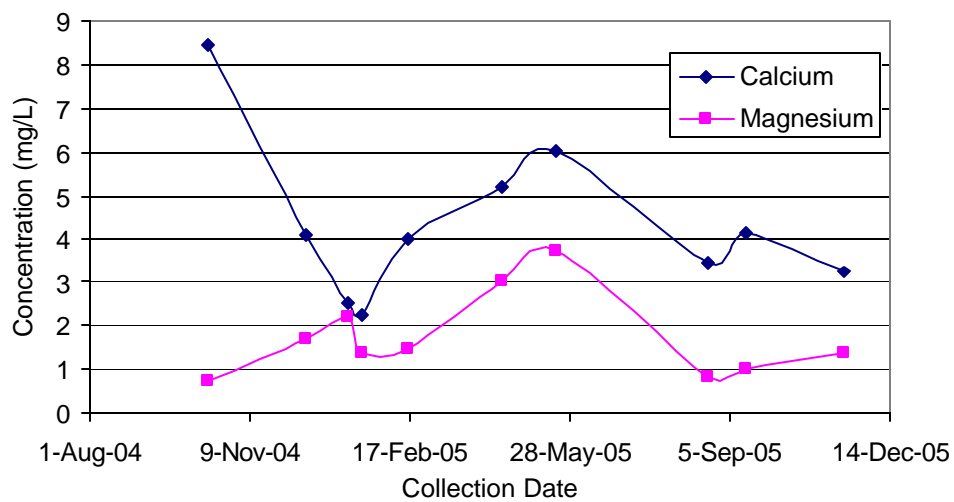
**Figure 4.4 Trends of Calcium and Magnesium for one Year of Sampling: for Samples Collected in October 2004 to November 2005**

Seasonal trends of calcium and magnesium mirror conductivity trends with regard to all sampling events except the results obtained in October 2004. Calcium and magnesium concentrations were greatest in the early spring sampling events. Calcium and magnesium trends show increase in the April and May 2005 sampling events reaching maximum concentrations in the May sampling month and then begin to decrease in the subsequent sampling months. Typically, the presence of calcium and magnesium is associated with underlying geology. Although this could still be attributable to the trends observed, it could also be due to a more direct surface flow phenomenon. The components of calcium and magnesium are important to the growth of trees. The fallen leaves would also contain these parameters and upon degradation, release these parameters which would then be picked up by the collection apparatuses.

**4.4.2 Seasonal Variation of Total Nitrogen, Nitrate, and Ammonia-Nitrogen**

The results from one year of sampling indicate that the concentrations of nitrogen and its components in the water samples vary with the time of year. The variation of nitrogen (total nitrogen, nitrate, and ammonia-nitrogen) is shown in Figure 4.5 and the variation of nitrogen and its components with collection method is in Figure 4.6.
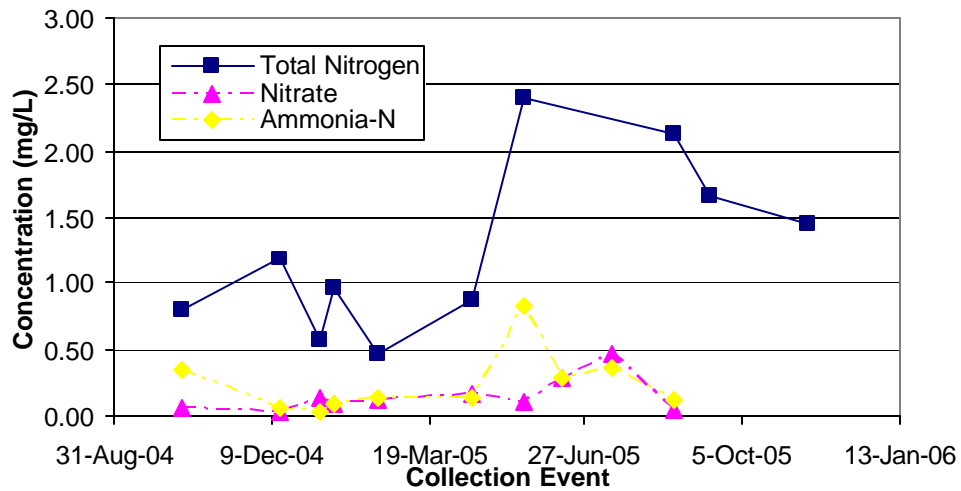
**Figure 4.5 Trends of Total Nitrogen, Nitrate, and Ammonia-Nitrogen for all Sampling Trips: October 2004 to November 2005**
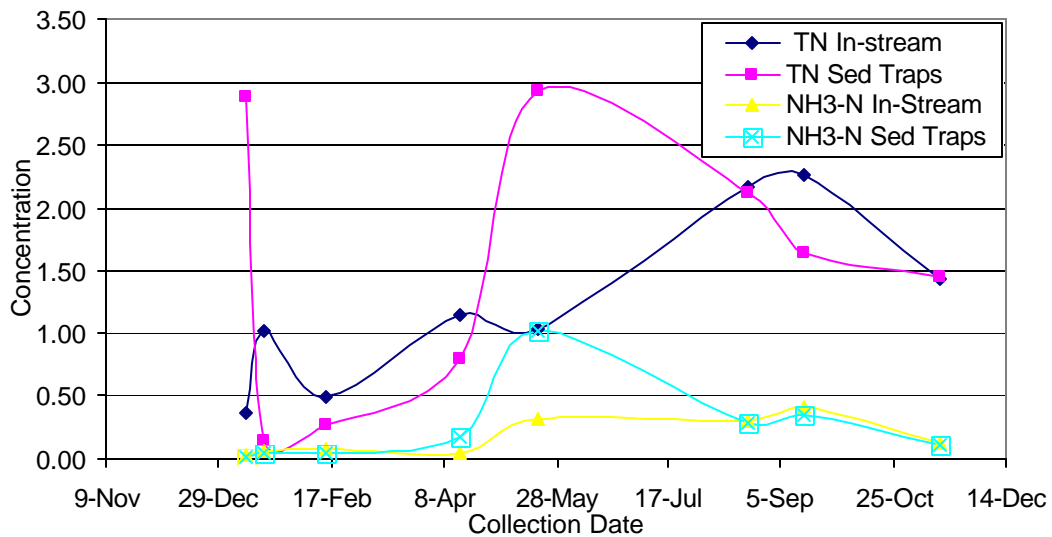


**Figure 4.6 Variability of Total Nitrogen and Ammonia-Nitrogen between Hillslope samplers and In-Stream Samples Collected During 2005**

All nitrogen constituents have lower concentrations in the winter months increases in the spring months to maximum concentrations in the May sampling event and then subsequently decrease. This trend mirrors the variation of nitrate documented in the Boston Mountain study (Lawson et al. 1985). The dramatic difference between total nitrogen and the components of nitrogen is explained by the presence of suspended solids that contain nitrogen. This explains the peak of total nitrogen in the February 2005 sampling event as further examined in Figure 4.8. This peak is similar to calcium and magnesium which was expected. The initial peak in calcium in the October sampling month resembles the trend in total nitrogen in Figure 4.6 and nitrate in Figure 4.7. In addition to these observations, Settergren et al. 1975 observed similar nitrogen fluctuations in the Ozark landscape.

Figure 4.6 is the seasonal variation of total nitrogen and ammonia for in-stream samples and hillslope sampler samples collected for the pre-harvest time period. Total nitrogen in the hillslope samplers had an initial peak in the October sampling event and decreased drastically during the winter months. The concentrations of total nitrogen increased in late winter early spring to peak in May with a concentration of 2.92 mg/L. The concentrations began to decrease through summer months and then leveled off in the November sampling event. Total nitrogen analyzed for in-stream samplers continually increased in concentration and peaked in the September 2005 sampling event. The trend displayed by total nitrogen collected in hillslope samplers is likely due to the breaking down of leaf matter which is collected directly by the hillslope samplers. Although, the trend displayed by total nitrogen from in-stream samplers is also caused by the decomposing of leaf matter it takes longer for the breaking down of leaf matter to reach

the ephemeral drainage channel. It has been documented in the Walker Branch study (Henderson et al. 1989) that sites have more leaf movement due to wind in various months in the year as a fraction of site aspect. This could also explain how the in-stream samplers collected more total nitrogen than the samples collected from hillslope samplers for the December 2004, both January 2005, the February 2005 and the April 2005 collection events.

Ammonia-nitrogen collected from in-stream samplers and hillslope samplers have unique trends. Ammonia-nitrogen collected from in-stream samplers is relatively constant before the May 2005 sample collection (Figure 4.6). With this collection time a steady increase occurs that remains constant until the November sampling period. The ammonia-nitrogen collected from the hillslope samplers are consistent with those samples collected from the in-stream samplers except for a peak of 1.0 mg/L that occurred in the May 2005 sampling period. This increase occurred at the same time as an increase in total nitrogen collected in the hillslope samplers. This indicates that rapid decomposition is occurring. The other component of nitrogen, nitrate, collected out of the hillslope samplers and in-stream samplers also show unique trends with regard to time of collection (Figure 4.6).
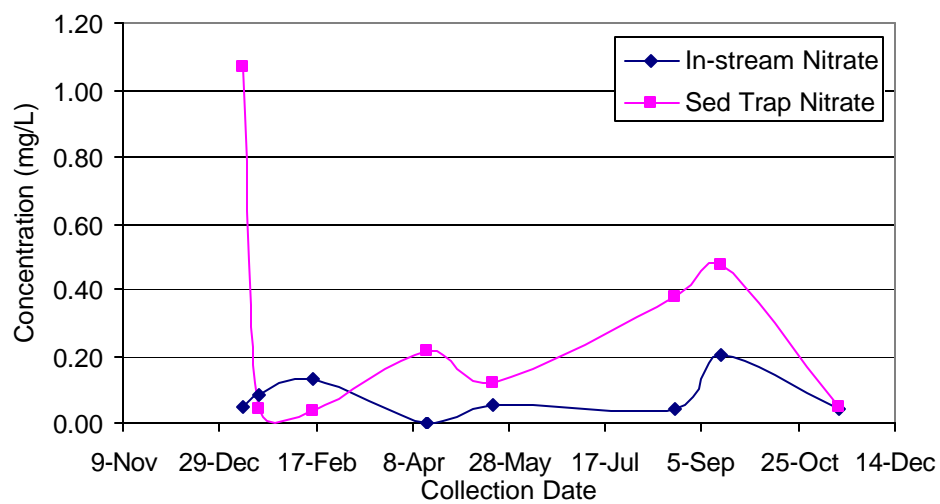
**Figure 4.7 Variation of Nitrate with Regard to Sampling Apparatus and Time of Collection: October 2004 to November 2005**

Average nitrate concentrations collected out of in-stream samplers are relatively constant throughout the year but have two distinct peaks: one occurring in the February sampling event and the other occurring in the September sampling event. Nitrate concentrations out of the hillslope samplers have a different trend. Nitrate concentrations had a peak in October 2005, as well as total nitrogen and calcium, and then plummeted in the winter months. The concentrations increased in the later winter into spring and summer and peaked in the September sampling event. Ammonia-nitrogen shared a similar trend but had the highest concentration a month earlier: A delay that could be due to nitrification. Sample concentrations collected out of in-stream samplers exceed those collected out of the hillslope samplers for the second January 2005 sampling date and the February 2005 sampling date. This could be due to two factors nitrate is very soluble an in times of great precipitation with no uptake the effluent would contain more nitrate. This has also been observed by Henderson et al 1989. The trends depicted by nitrogen and its components are similar to the variation of potassium with the time of collection.

**4.4.3 Variation of Potassium with Collection Time**

Potassium, although does not take part in decomposition, has been shown to be released due to decomposition. This observation is in Figure 4.8. The variation of potassium in regard to sampling apparatus is in Figure 4.9.
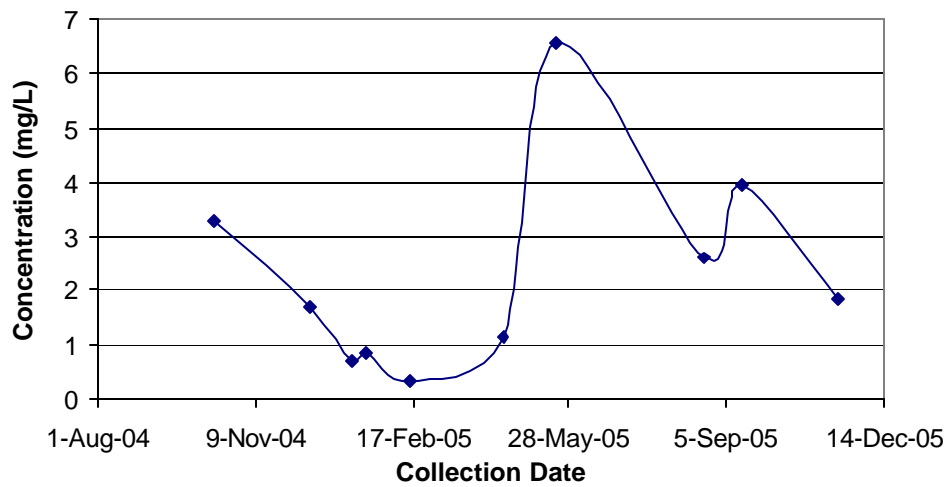
**Figure 4.8 Trends Regarding Average Potassium Concentrations for all Samples Collected based upon time of Collection: October 2004 to November 2005**
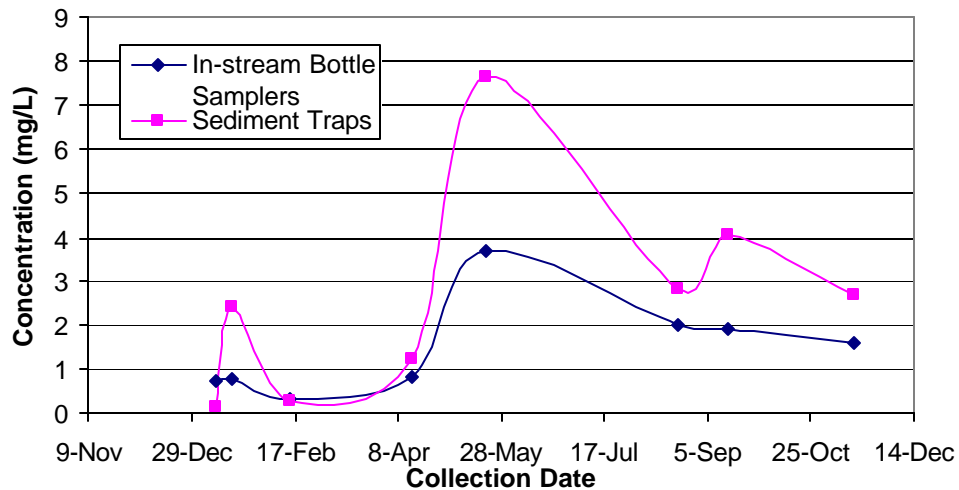


**Figure 4.9 Variability of Average Potassium Concentrations between Hillslope samplers and In-stream Bottle Samplers for Samples Collected During 2005**

Potassium follows the trend aforementioned – less is collected in the winter to a minimum average of 0.3 mg/L. The concentrations increase in early spring and reach a maximum value of 6.5 mg/L in the May 2005 sampling event. Potassium concentrations then decrease in the summer to a concentration of 2.8 mg/L, rebounds in the September 2005 sampling event and declines in the late fall. This trend coincides with potassium concentrations discussed in the Boston Mountain study (Lawson et al. 2005). This trend better indicates the decomposition process when looking at differences in concentrations of potassium in samples obtained from hillslope samplers and in-stream samplers (Figure 4.9). Potassium analyzed in water samples collected in hillslope samplers is at higher concentrations that potassium collected from in-stream samplers. The only time when this was not valid was during the winter period when microbe and plant activity would be at its lowest (Henderson et al. 1989). This is due to the hillslope samplers being closer to the site of detritus degradation. The peak of potassium collected in both instruments is the same sample collection date as pH, conductivity, and total nitrogen. Potassium concentrations then decrease in the summer months. This trend is due to a fixed amount of leaf matter that has already decomposed. Pope, 1977 documented that over a half of all leaf matter is decomposed by June in most humid continental mixed hardwood forests. A peak in potassium concentrations collected in hillslope samplers occurred in the September collection event which would correspond with the local deciduous trees beginning to shed leaves. The same trends documented in nitrogen, potassium, pH and conductivity is evident in the seasonal variation of phosphorous.

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**4.4.4 Seasonal Variation of Total Phosphorous and Soluble Reactive Phosphorous**

Phosphorous is a limiting nutrient in many forest ecosystems. A limiting nutrient refers to a nutrient that limits plant growth. In the Ozarks, phosphorous was found to be negligible in soil horizons below the A-horizon. Phosphorous concentrations in the Ozarks were found to exceed the concentrations documented in the Walker Branch watershed (Henderson et al. 1989), but were close to the ephemeral drainage ways monitored in the Boston Mountain study (Lawson et al. 1985). The reason for this correlations maybe better understood by looking at the seasonal trends of the average concentrations of total phosphorous and soluble reactive phosphorous for all samples collected (Figure 4.10) and for the variation of total phosphorous and soluble reactive phosphorous with regard to in-stream samplers and hillslope samplers (Figure 4.11).
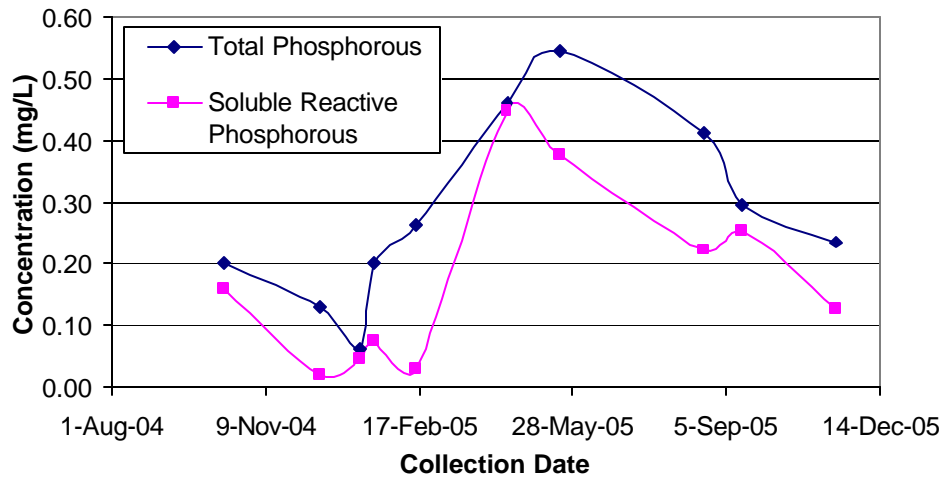
**Figure 4.10 Seasonal Trends Regarding Total Phosphorous and Soluble Reactive Phosphorus for all Samples Collected: October 2004 to November 2005**
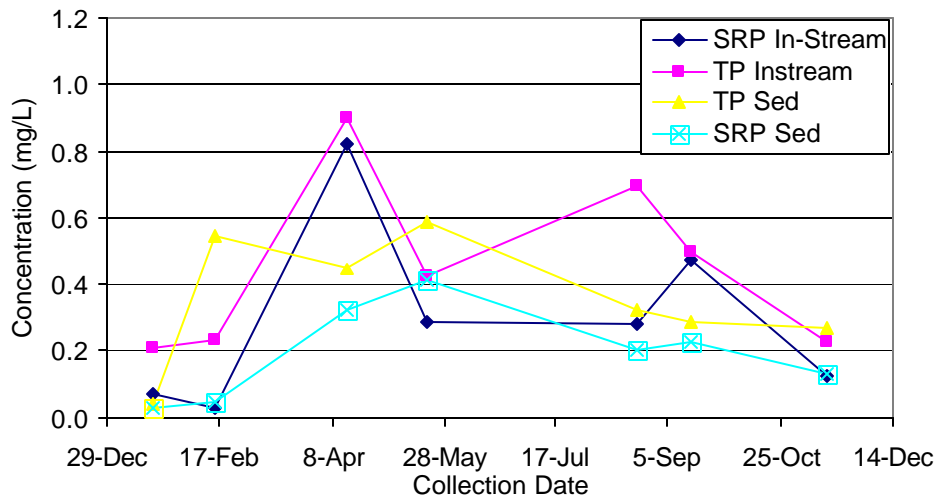


**Figure 4.11 Seasonal Trends Regarding Total Phosphorous and Soluble Reactive Phosphorous for In-Stream samplers and Hillslope samplers: From October 2004 to November 2005**

Total phosphorus had a maximum average concentration of 0.54 mg/L in the May 2005

sampling event and a minimum average concentration from the January 10, 2005

sampling event with a concentration of 0.08 mg/L. Soluble reactive phosphorous had a

maximum concentration during the April 2005 sampling event with a 0.46 mg/L average

and had the lowest average concentration 0.02 mg/L. Both parameters show similar

trends. The concentrations increase in late winter early spring. They reach a maximum

concentration in the spring sampling months and then begin to decrease in the fall

months. This trend does not coincide with Walker Branch (Henderson et al. 1989) but

does coincide with the Boston Mountain study (Lawson et al. 1985). Once again, in the

Boston Mountain study (Lawson et al. 1985) higher amounts of phosphorous were

reported in the fall months coinciding with fallen leaves. The concentration then

decreases in winter and begins to increase in spring months and decreases in summer

months. This observation however, does not coincide with Figure 4.11. The samples

collected from the in-stream collection apparatuses have higher peaks than collected out

of the hillslope samplers. This could be attributed to deep seepage that has been observed

in Settergren et al. 1972. The greatest peaks in total phosphorous and soluble reactive

phosphorous occurs in the February 2005 and May 2005 sampling events. The peak in

the May 2005 sampling event agrees with the peaks of potassium and nitrogen. The

February sampling event not only has the greatest peak in total phosphorous but has a

small concentration of soluble reactive phosphorous. The difference in these two

parameter concentrations could be due to the collection of total suspended solids. A

highlighted explanation of total suspended solids is in Section 4.4.5.

**4.4.5 Seasonal Variation of Total Suspended Solids and Organic Suspended Solids**

Amounts of TSS and TVSS vary upon many parameters including: precipitation intensity, precipitation amount, amount of litter or detritus on the forest floor, amount of decomposition of the detritus, and presence of a forest crown. The combined effects of these variables resulted in the seasonal trend for TSS and TVSS for the Missouri Ozarks study as shown in Figure 4.11.
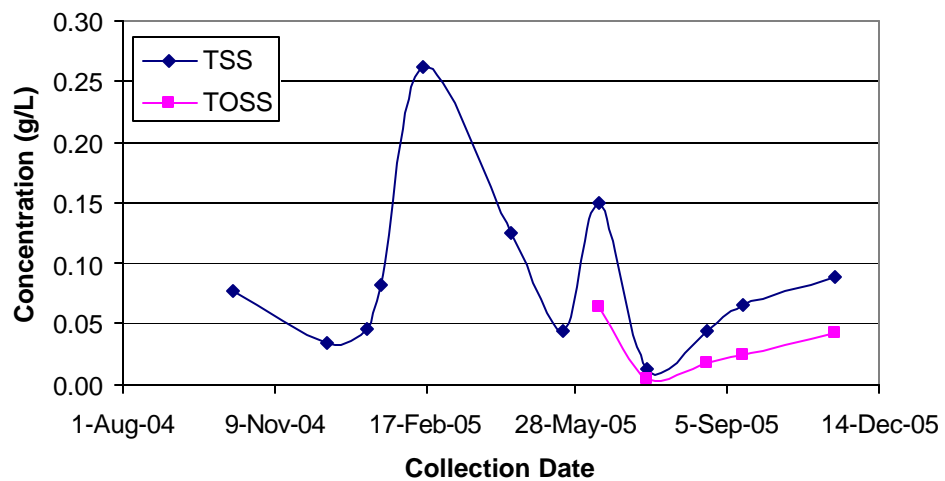
**Figure 4.11 Seasonal Trends Regarding TSS and TVSS for all Samples Collected:**
**October 2004 to November 2005**

Total suspended solids decreased after the initial October sampling event and reached a minimum average of 0.03 g/L in the December sampling event. Total suspended solids increased in concentration and peaked in the February sampling event; once again decreased, then peaked in the June sampling event. Total suspended solids decreased once more and then begun to increase for three consecutive sampling months. The peak in June is thought to be a false positive due to an initial collection of hillslope sampler water samples and then using the collected sample to wash the remaining sediment or residual material out of the catchments. This re-introduced sample was then collected. No in-stream water samples were collected in the June sample collection event. The increase in total suspended sediment in the January sampling events and in the events in late fall of 2005 is due to a combination of no crown cover, and heavy intense precipitation events that more readily move sediment. Following this explanation, the February sampling event not only has the highest average but also has the highest amount of TSS collected from it – 1.14 g/L from site CR7-6 water sampler 5 at the 0 inch collection apparatus. The trends depicted in Section 4.4 are in close agreement to Settergren et al. (1972), a study conducted on four watersheds in the Missouri Ozarks. Settergren et al. (1972) showed that high yields of ammonia, phosphorous, potassium, calcium, and nitrogen occur most frequently in summer and early fall months as the nutrients are picked up by rainfall from the tree foliage and decomposing matter.

**4.5 Parameters that Vary with Site (Spatial Variation)**

All parameters were analyzed on a site variability basis. For all sites, the water samples collected range greatly. The following sections will document this site variation with regard to the following parameters: electrical conductivity, calcium, magnesium, nitrate, total nitrogen, ammonia-nitrogen, potassium, and total suspended solids. The parameters of pH, soluble reactive phosphorous, and total phosphorous did not range to the magnitude of the selected parameters. Total volatile suspended solids followed the trend of total suspended solids.

**4.5.1 Spatial Variation of Electrical Conductivity, Calcium, and Magnesium with Site for all Water Samples Collected for All Sites**

Even though pH did not vary greatly among sites, the parameters of electrical conductivity, calcium, and magnesium did. The variation of electrical conductivity among all sites is shown in Figure 4.12. Angeline sites had an average of 48 us/cm, a standard deviation of 59 us/cm, a coefficient of variation (c.o.v) of 1.2 and a maximum electrical conductivity of 432 us/cm at site A17-2. Current River had an average electrical conductivity of 43 us/cm, a standard deviation of 41 us/cm, a c.o.v of 0.98 and a maximum electrical conductivity of 244 us/cm. Samples with the highest conductivity level were from the Angeline sites.

Unpublished data from Mueller (2006) describes that the study sites have a difference in geology. The presence of a sandstone geologic layer over the Angeline sites could produce an aquifer. The aquifer would entrap water within the dolomite layers thus increasing residence time. Observations for several sites in Angeline during a rainstorm event indicate seepage flow from similar elevations along slopes, thus indicating lateral

subsurface flow across textural or structural boundaries (geologic strata or textural breaks in soils). Water appeared more turbid upstream (before entering) losing stretches than where it emerged. This could indicate that filtering is occurring below ground and weathering may be occurring that would further enhance conductivity or calcium and magnesium amounts. Samples containing larger conductivity were collected from in-stream samplers further down the instrumented stream channel. Figure 4.13 displays the occurrence of conductivity levels from both management areas.
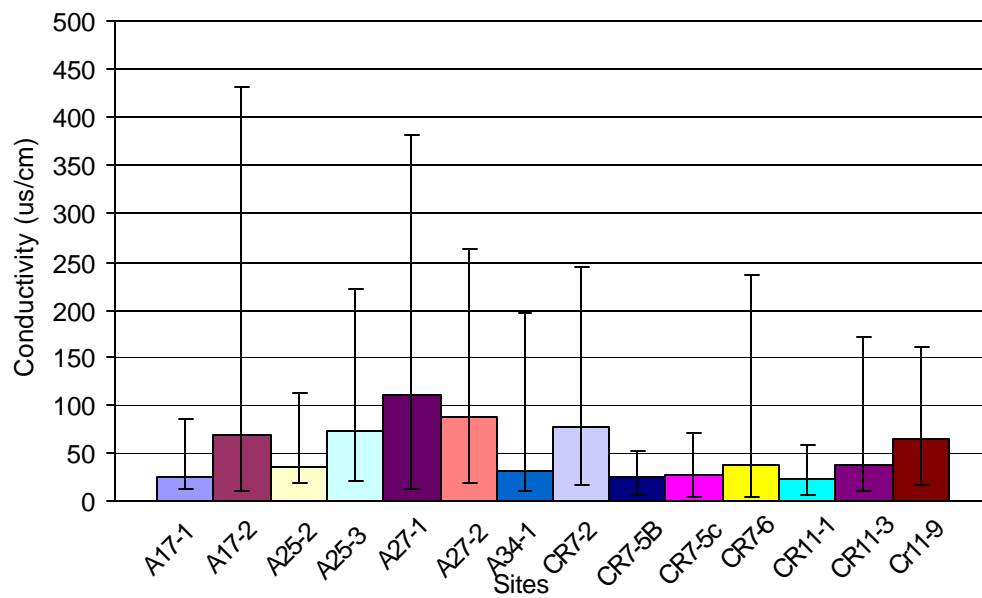
**Figure 4.12 Variation of Electrical Conductivity with Site for all Water Samples Collected: October 2004 to November 2005**
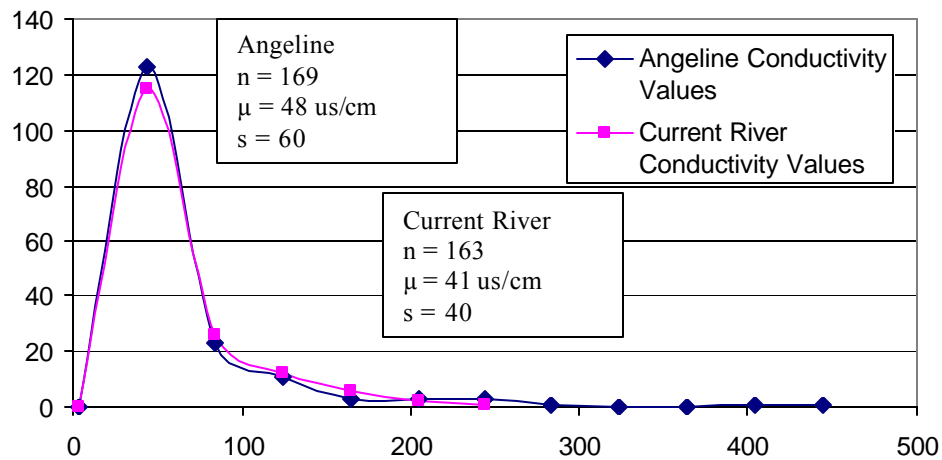


**Figure 4.13 Number of Occurrences of Electrical Conductivity versus the sample originations - Angeline or Current River Conservation Areas**

Figure 4.13 shows that the trends of the levels of electrical conductivity are similar for both conservation areas. The samples from the Angeline sites that exceed the maximum concentrations from Current River sites originate from in-stream samplers further down the instrumented stream channel. Variable soils could also lead to higher amounts of conductivity in Angeline Sites than Current River Sites (Hammer, 1997). The data given is further explored by the occurrence of magnesium and calcium in Figure 4.14.
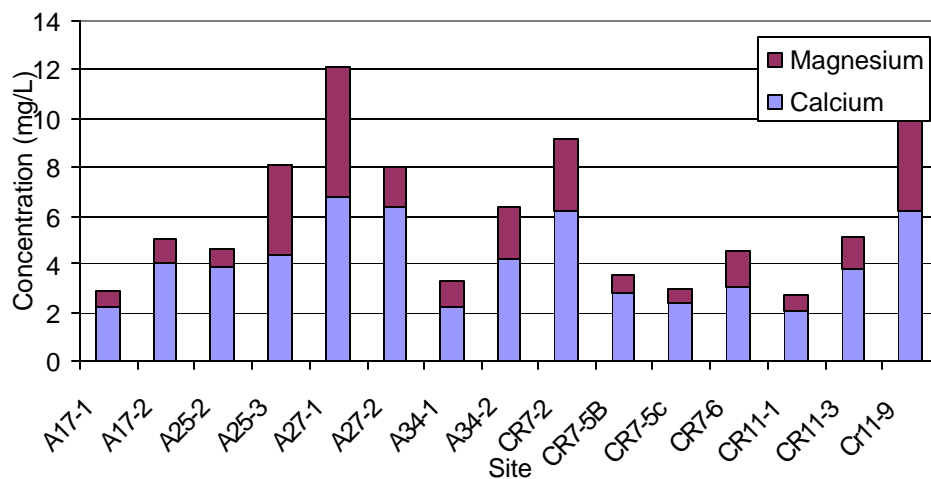
**Figure 4.14 Variation of Calcium and Magnesium among Sites for all Water
Samples Collected:  October 2004 to November 2005**

The trend depicted in Figure 4.14 overlays very well with average concentrations pictured in Figure 4.12. This trend is expected since calcium and magnesium are two cations that are included in conductivity measurements. Either site geology is playing a part in increased concentrations, or leaves on Angeline sites have more calcium and magnesium. Moreover, since there were not any trend differences in the concentrations of calcium and magnesium with instrument type, then the latter (Angeline leaf matter contains more calcium and magnesium) is a reason for the increased calcium and magnesium values. Leaves from both areas could be collected and analyzed for multiple nutrients including calcium and magnesium.

**4.5.2 Variation of Total Nitrogen, Ammonia-Nitrogen, and Nitrate with Site**

Total nitrogen and its components varied greatly within each site and from site to site as shown in Figure 4.15 and 4.16.
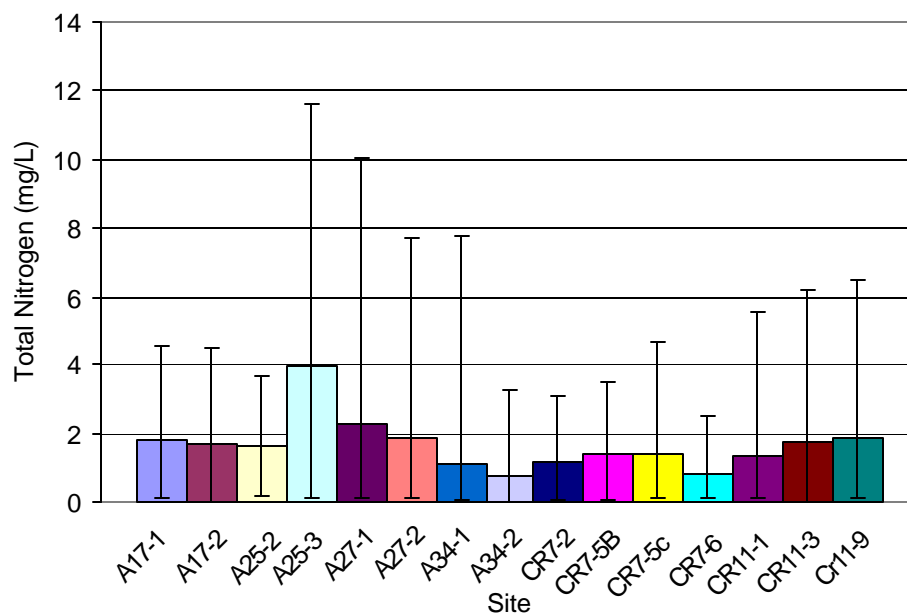
**Figure 4.15 Variation of Total Nitrogen for all Samples Collected: October 2004 to November 2005**
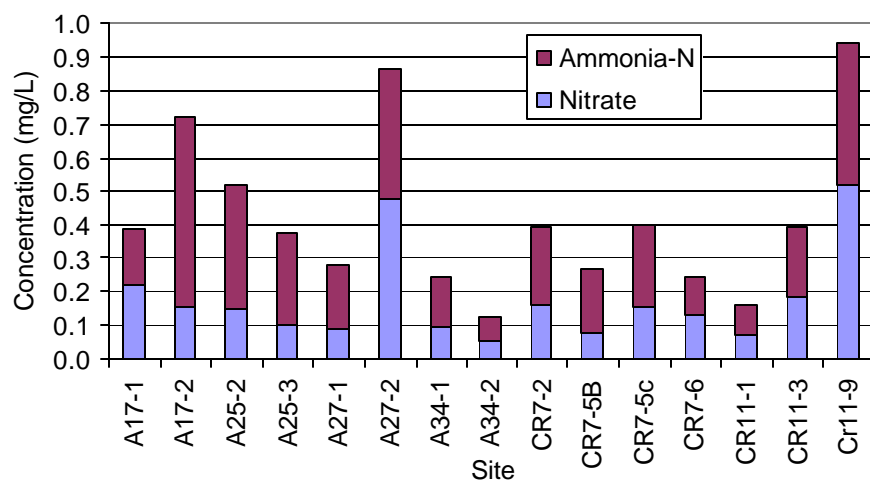


**Figure 4.16 Variation of Ammonia-Nitrate and Nitrate with Site for all Samples Collected: October 2004 to November 2005**

Most concentrations varied from close to the detection limit 0.01 mg/L, to about 4 mg/L. The lower concentrations of total nitrogen primarily were from in-stream bottle samplers. As with conductivity, Angeline sites have a greater average concentration of total nitrogen than Current River Sites. A similar trend is depicted in Figure 4.11 for ammonia-nitrogen and nitrate. Ammonia-nitrogen and nitrate vary greatly from site to site. Average nitrate concentrations varied from 0.1 mg/L in site A34-2 to above 0.7 mg/L in site A25-3. As with total nitrogen, nitrate was found to be slightly elevated in the Angeline sites. This holds true for all site but site CR11-9. Ammonia-nitrogen had trends similar to nitrate's trends. The average reported concentrations ranged from under 0.1 mg/L to nearly 1 mg/L in A25-3. It can be noted that the concentrations of total nitrogen, ammonia-nitrogen, and nitrate are similar to the concentrations documented with conductivity. This similar trend was reported by Lawson et al. 1985.

### 4.5.3 Variation of Potassium with Site for all Samples Collected

A wide variation of potassium concentration was encountered for all sites and within individual sites. This trend is shown in Figure 4.12. Typical values ranged from 0.01 mg/L to nearly 11 mg/L. Angeline sites on average had higher potassium concentration in the samples with a concentration of 2.3 mg/L. Current river sites averaged nearly 2.2 mg/L. It has been found that the sites that had the highest levels of potassium were sites that collected this potassium in hillslope samplers. This makes sense since the highest amounts of potassium originated from hillslope samplers. Due to this, the amount of leaf litter in a hillslope samplers, and therefore, the location of the hillslope samplers with regard to overstory vegetation and slope percent, an important attribute to the collection of hillslope samplers samples in Section 4.5.4, are of great

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importance.   This can be illustrated by a specific example.   The highest potassium concentration water sample was derived from a hillslope sampler from site CR7-2.  This potassium concentration in this sample was found to be 18 mg/L.  The hillslope sampler is located near the edge of the monitored stream at a 43 % slope with a heavy overstory of deciduous trees. The rest of the highest potassium concentrations mimic this example.
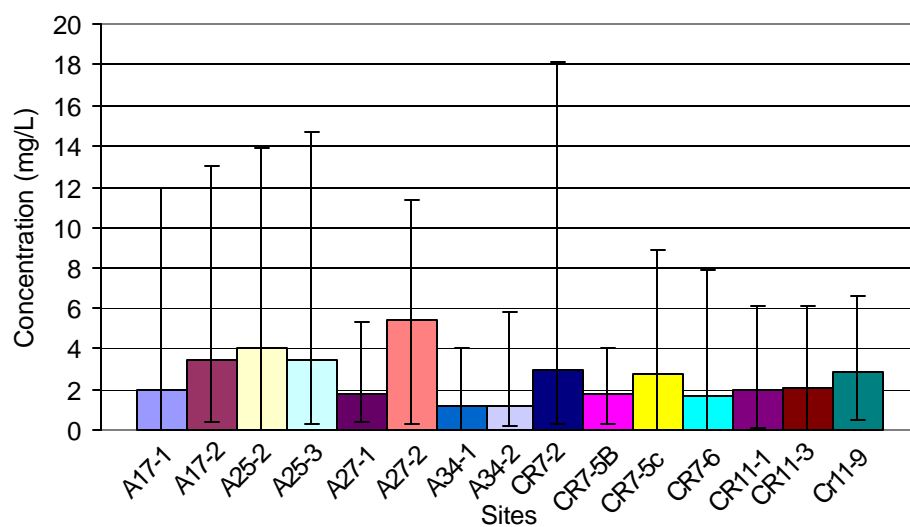
**Figure 4.16 Variation of Potassium with Site for All Samples Collected: October 2004 to November 2005**

**4.5.4 Variation of Total Suspended Solids with Site for all Samples Collected**

Total suspended solids concentrations also varied within a particular site and with regard to surrounding sites (Figure 4.17). Average sample TSS concentrations vary between 0.13 g/L and 0.06 g/L in the Angeline Sites whereas average TSS concentrations vary between 0.16 g/L to 0.04 g/L in the Current River sites. Site CR7-6 has the greatest average of total suspended solids and also the greatest maximum concentration as well. This could be attributed to the steep slopes of the site resulting from deep incision of the channel's main ephemeral stream bed. The relation of instrumentation to total suspended solid concentrations is shown in Figures 4.14 and 4.15.
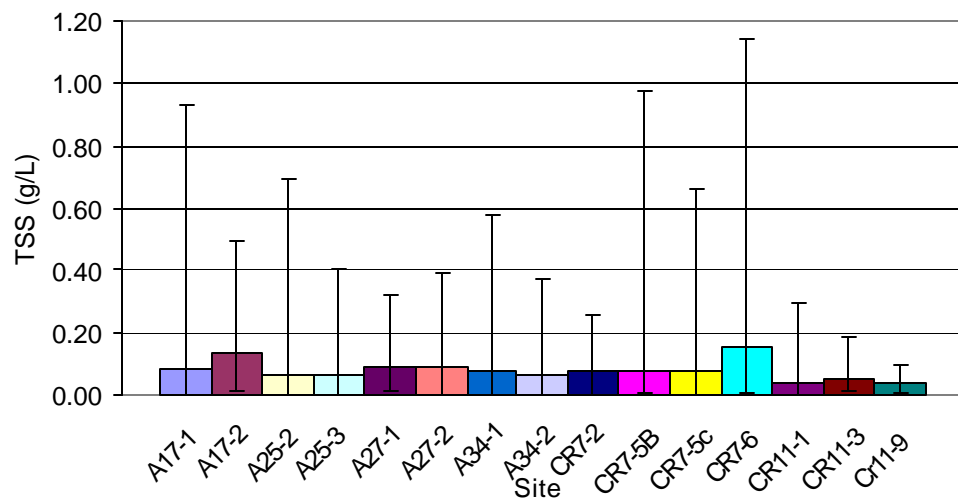
**Figure 4.13 Variation of Average TSS Concentrations Bounded by the Range of Concentrations with regard to Site: October 2004 to November 2005**

The effect of location of in-stream water samplers in the measured TSS is shown in Figure 4.14 for Site A34-1. The TSS results of 26 in-stream samples are represented in Figure 4.14. The further downstream the samplers are the more total suspended solids are being collected. This trend has been somewhat defined for the in-stream samplers on site A34-1. Even though the plot is represented by a linear trend, in actuality micro-stream variability such as channel shape (amount of incision) or elevation in the landscape that has been correlated to underlying geology (Mueller, 2006) is very important in the amount of TSS collected. Sites A17-1, CR7-5B, CR7-5C, and CR7-6 all show similar trends. All of these sites have evidence of channel incision that would relate to a more active stream system. Mueller (2006) has cataloged the amount of incision by the use of profiles of the instrumented ephemeral channel. The effect of slope percent on total suspended solid is in Figure 4.15. The effect of the surface slope at the hillslope samplers on the TSS concentration is shown for three sampling events in Figure 4.15. For all three sampling events, the greater the slope of the hillslope sampler the more total suspended solids were collected. It can also be noted that as the precipitation event increased in precipitation amount and/or intensity the amount of total suspended solids. The August sampling event had the greatest amount of collected TSS as well as the greatest amount of linearity. The August sampling event also had the greatest precipitation event with nearly 9 cm. The trend of increasing TSS with increasing precipitation event follows for the two other sampling events. It has been observed that this trend occurs more readily on Angeline sites than Current River sites. A possible explanation for this could be that the location of the hillslope sampler was planned for the Angeline sites and the hillslope sampler were place on equal spacing without regard to

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landform placement or slope inclination.  Similar results were gathered by (Holy, 1980).

Various factors could also affect the amount of total suspended solids off of slopes

including:  the slope length (Lima, 1965), slope shape (Lima and Molen, 1988), and slope

exposure (Lima, 1989).
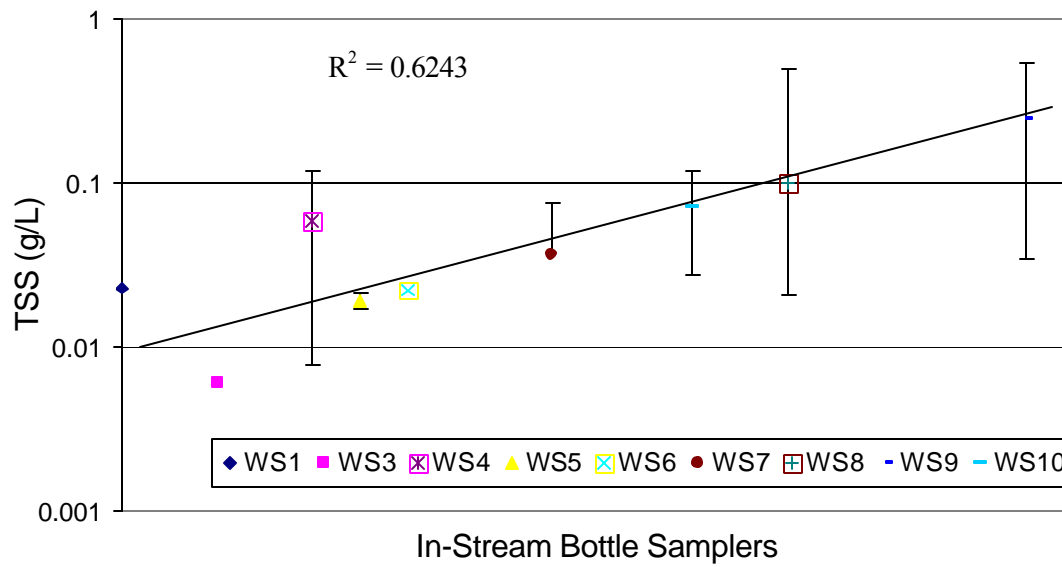
**Figure 4.14 Variation of Total Suspended Solid Concentrations for Average Concentrations for In-Stream Samplers for Site A34-1. WS1 is at the head of the perennial stream and WS9 is at the bottom of the basin. The points are spaced according to their spatial location in the instrumented channel**
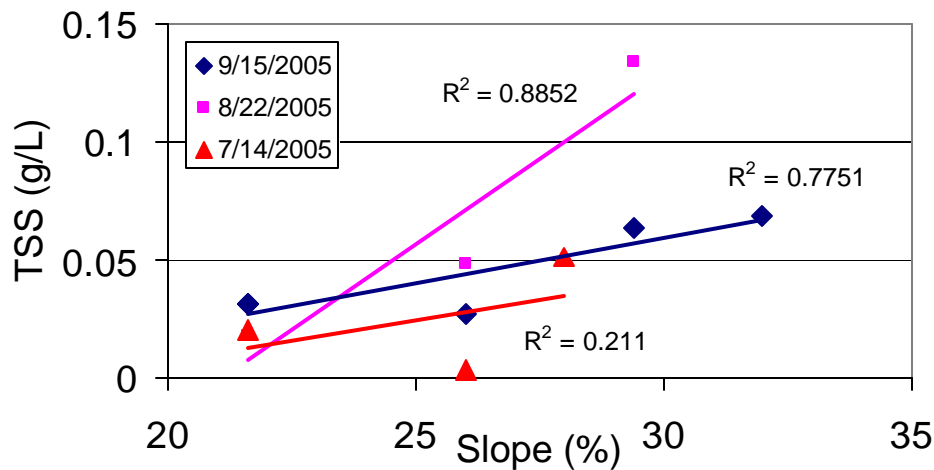


**Figure 4.15 Variation of Total Suspended Solid Concentrations for Average Concentrations for Hillslope samplers**

**4.7 Summary**

The main objective of this thesis was to document baseline water quality by analyzing 12 parameters and to establish initial trends for all parameters. The first year of water sampling in the Missouri Ozarks yielded 384 samples from 13 sampling events. The samples originated from all 15 sites and hillslope samplers and in-stream water samplers. Sixty-nine hillslope and 91 in-stream samplers have been installed on the 15 study sites.

Potassium, nitrogen and its compounds, phosphorous, soluble reactive phosphorous, calcium, magnesium, pH, conductivity, and TSS all showed trends regarding the time the samples were collected. The nutrients potassium, nitrogen, nitrate, ammonia-nitrogen, and pH all have similar trends indicating that the samplers are picking up decomposition in the forest floor. This trend is related to concentrations being higher in hillslope samplers than in in-stream samplers. Conductivity, calcium, and magnesium also have similar trends. However, these parameters do not differ by sampling apparatus. Therefore, hydrological reasons, including seepage and underground flow, may be the cause for their variation with season. The trend in the variation of total suspended solids indicated that a multitude of factors including crown density and precipitation event may cause greater concentrations of TSS. Parameters were also found to vary within a site and with regard to other sites.

Electrical conductivity, calcium, magnesium, nitrogen and its components, potassium, and total suspended solids were compared on a site by site basis. Water samples from Angeline sites were found to have higher electrical conductivity and as such more calcium and magnesium than the samples collected from the Current River

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sites.  Geologic and hydrologic factors could be the reason, or perhaps the decomposing leaf matter in Angeline sites contained more of these constituents than the Current River sites.  Differences in parent material may also contribute to the differences.  Nitrogen and its components were found to vary the same as calcium and magnesium; however, the higher concentrations were found to occur in the  hillslope samplers.  Total suspended solid concentrations were also found to vary within a site and with regard to multiple sites but micro-variations with sites also experienced trends.  These micro-topographic variations do not occur in every site, due to differences in  hillslope sampler placement and stream hydrology.  Due to  the variations of concentrations for all parameters the three sigma method  (Duncan, 2002) was selected as a way to quantitatively select baseline concentrations.

## Chapter 5 - Practical Implications

## 5.1 Introduction

The objective of this thesis was to quantify selected pre-harvest concentrations for 12 different water quality parameters in fifteen forest watersheds located in the Missouri Ozarks that are marked for regenerative oak clearcut. The parameters include: pH, conductivity, total suspended solids, total volatile suspended solids, calcium, magnesium, potassium, total phosphorous, soluble reactive phosphorous, ammonia-nitrogen, nitrate, and total nitrogen. Due to variability in precipitation event, season, stream hydrology, site geologic conditions and other factors, the concentrations of the 12 selected parameters vary greatly among the water samples collected. To establish a quantitative baseline value but also accommodate for these variations, the three sigma method (Duncan, 2002) was used. The method was illustrated in Section 5.2 and the resulting baseline values are shown in relation to concentrations from other studies. A comparison of samples from the hillslope and in-stream samplers is located in Section 5.3. Concentrations of water samples collected from site instrumentation versus concentrations obtained from grab samples is presented in Section 5.4. The importance of including the hillslope and in-stream samplers for the three sigma value for each parameter is in Section 5.5. The importance of these quantitative baseline water quality values is summarized in Section 5.6.

## 5.2 The Three Sigma Method

Table 5.1 contains the baseline values for the 12 water quality parameters (pre-harvest) as determined using the three sigma method. The results are compared to those from the Walker Branch and Boston Mountain Studies as presented in Sections 2.3 and 2.4 respectively. The concentrations calculated using the three sigma method serve as reference points to ascertain the effect of timber harvesting on headwater ephemeral drainage basins and will help determine the overall effectiveness of Missouri Department of Conservation's best management practice. The method is depicted in Figure 5.1 with total suspended solids for all water quality data collected from October 2004 to January 31, 2006. Figure 5.1 is the distribution of total suspended solids for all samples collected and plotted with regard to the number of observations for a particular concentration. The observed trend is lognormal. The standard deviation is 0.14 g/L and the coefficient of variation (the standard deviation divided by the mean) is 1.73. The magnitude of the standard deviation is greater than the magnitude of the mean. Indicating the large variability in the amount of total suspended solids collected. The distribution plots for the eleven remaining constituents are located in the Appendix 12.
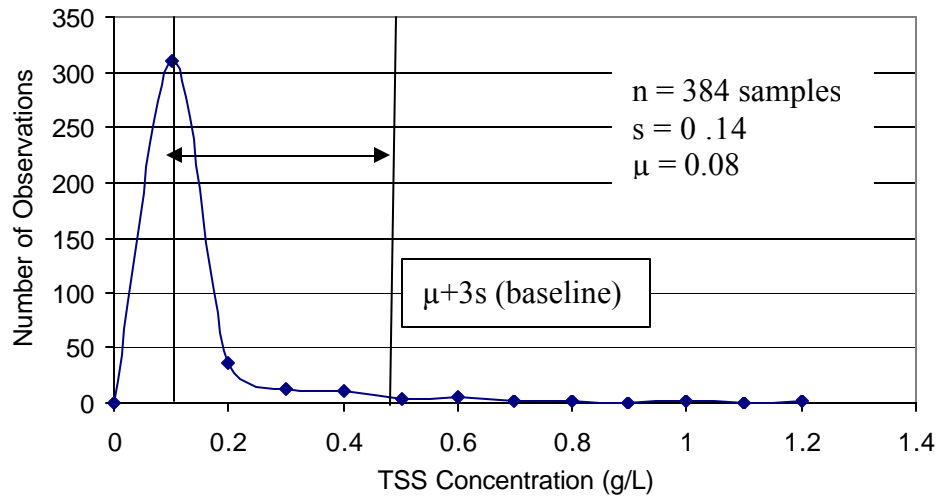
**Figure 5.1 Three Sigma Method for Total Suspended Solids for all Samples (In-Stream and Hillslope) Collected from October 2004 to November 2006 at total of 384 samples**

**Table 5.1: Comparison of the Baseline Concentrations of Water Quality Parameters with the values from the Walker Branch Watershed Project and the Boston Mountain Project**

| Parameter | Ozark Study (1) (2004 - 2006) | | | Walker Branch (2) (1970-1974) | Boston Mountains (3) (1974 - 1981) |
|---|---|---|---|---|---|
| | mean μ | std dev s | Baseline 3*s+μ | | |
| pH | 6.19 | 0.72 | 8.30 | NA | 5.96 |
| Cond (us/cm) | 45.33 | 51.43 | 199.61 | NA | 21.17 |
| TSS (g/L) | 0.08 | 0.14 | 0.50 | NA | NA |
| TOSS (g/L) | 0.03 | 0.05 | 0.18 | NA | NA |
| Ca (mg/L) | 3.62 | 3.13 | 13.01 | 16.00 | 0.51 |
| Mg (mg/L) | 1.60 | 2.81 | 10.04 | 8.40 | 0.43 |
| K (mg/L) | 2.27 | 2.70 | 10.38 | 0.73 | 0.92 |
| TP (mg/L) | 0.26 | 0.35 | 1.30 | NA | 0.18 |
| SRP (mg/L) | 0.16 | 0.31 | 1.08 | 0.0023 | NA |
| NH3-N (mg/L) | 0.22 | 0.48 | 1.67 | 0.06 | 0.34 |
| NO3 (mg/L) | 0.16 | 0.39 | 1.33 | 0.03 | 1.93 |
| TN (mg/L) | 1.43 | 1.45 | 5.80 | 0.16 | NA |

1. Ozark Timber Harvest Project (Values represent a composite of water samples from in-stream and hillslope samplers
2. Walker Branch Watershed Project – Henderson, Johnson  (Henderson et al, 1989)
3. Boston Mountain project in Arkansas (Lawson et al, 1985)

Listed in Table 5.1 are the results using the three sigma method for all parameters selected in the timber harvest study. pH has a mean of 6.19 and when the three sigma method is applied, the baseline value is 8.3. The mean pH is close to the documented Boston Mountain (Lawson, 1985) values and the three sigma method value is close to that documented by the Walker Branch Watershed study (Henderson et al. 1989). A pH value of 8.3 is the pH of water that has been buffered by calcareous rock, which follows since dolomite is dominant in the sites of the Ozark timber harvest study as well as the Walker Branch sites. Furthermore, the mean electrical conductivity value of 45 us/cm and the background concentration of 199 us/cm are also greater than the values documented by the Boston Mountain (Lawson et al. 1985) study. The differences in geology – the Ozarks have dolomite and the Boston Mountain's study sites have a dominant sandstone geology or variability of soils that is a common occurrence in both the Ozark study and the Walker Branch study (Hammer, 1997; Henderson et al. 1989). The concentrations of calcium and magnesium fit within the range documented by the two studies from the literature and also support the presence of dolomite having an effect on the samples collected.

Mean potassium concentrations collected in the Ozarks have a concentration of 2.27 mg/L, far greater than the concentrations in the Walker Branch (Henderson et al. 1989) and the Boston Mountain studies (Lawson et al. 1985). The three sigma value for potassium in the Ozarks study is 10.38 mg/L. In the Ozark study, this high level of potassium is due to leaf degradation in the hillslope samplers.

Total phosphorous and soluble reactive phosphorous also fit within the range of the various studies. A mean of 0.26 mg/L and a three sigma method concentration of 1.3

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mg/L was found for the Ozark sites.  The mean is close to the mean (0.18 mg/L) collected in the Boston Mountain (Lawson et al. 1985) study.   This is attributed to both sites studying ephemeral streams, or surface flow as it moves through organic matter.  Soluble reactive phosphorous originating from the sites in the Ozarks had a mean of 0.16 mg/L and a three sigma concentration of 1.08 mg/L.  These levels are 100 to 1000 times higher than those found in Walker Branch watershed (0.0023 mg/L) (Henderson et al. 1989).

Total nitrogen and its components share the same trends.  Ammonia-nitrogen collected in the Ozarks has a mean of 0.22 mg/L and a three sigma value of 1.67 mg/L. The mean value is similar to the mean value found at the Boston Mountain study (0.34 mg/L) (Lawson et al. 1985).  However, nitrate did not share in ammonia's relative high concentration.  The average nitrate concentration in the Ozarks was 0.16 mg/L and the three sigma method concentration is 1.33 mg/L.  The three sigma concentration is closer to the concentration of nitrate found in the Boston Mountain study (1.93 mg/L) (Lawson et al. 1985). All concentrations of nitrogen compounds are orders of magnitude higher than found at Walker Branch Watershed (Henderson et al. 1989).   Total nitrogen collected in the Ozarks had a mean concentration of 1.43 mg/L and a three sigma concentration of 5.8 mg/L.  The mean value is an order of magnitude greater than that found at Walker Branch (Henderson et al. 1989).  As more pre-harvest (baseline) data becomes available the three sigma method values can be updated.  Another aspect that must be taken into account is the difference in concentrations obtained from the in-stream and hillslope samplers.

**5.3 Comparison between Concentrations of Parameters Derived from Hillslope and In-Stream Samplers**

In Chapter 4, there was much discussion regarding seasonal variability and some aspect of this variability was shown to be attributed to the difference in concentrations collected from in-stream and hillslope samplers. In addition to these observations, not only have the hillslope samplers collected more samples after their retrofits, but it has been held suspect that hillslope flow occurs in forest watersheds due to macro pores in soil structure. Due to these considerations, a comparison was made between the hillslope three sigma concentrations and the in-stream three sigma concentrations. Concentration variations between the two sampling apparatuses are located in Table 5.2 and Table 5.3 and in Figure 5.2.

Theoretical hydrology in a forested watershed has dictated that surface flow only occurs in times where precipitation intensity and duration are greater than the storage potential of the soil at a particular time in the season (Horton, 1933). This theory was supported by observations that rarely does overland flow occur in a forested watershed (Chorley, 1978). Similar observations were made during field work in the Ozarks project. However, these initial observations helped form a theoretical model of forest hydrology called the Variable Source Area model (Horton, 1933). This dictates that channel flow in a forested watershed is due to concentrated underground seepage and the attributing source for this flow increases into smaller ephemeral drainage ways if the precipitation event has a great enough intensity, duration, or if there is enough antecedent moisture in the soil. Surface runoff was still dictated by the philosophy of saturation of the top layers of soil (Chorley, 1978). However, newer models of forest hydrology

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indicate that surface flow may be further negated due to piping channels and through biologically created non capillary channels (Jones, 1971). These avenues of flow would undermine the effectiveness of the hillslope samplers – especially since the traps only collected 9 out of a total of 177 samples before the retrofits went into effect. However, in the present study, field observations indicate that hillslope flow could have escaped capture due to poor contact between the collection trough and the ground surface (Bunger, 2005). The problem was corrected with a retrofit that included using a 2 ft wide plastic sheet to seal the contact with the ground surface. Hillslope control samplers were installed to document the effect of the 2 ft wide plastic strip.

**Table 5.2: Baseline (Pre-Harvest) Concentrations for Samples collected from In-Stream Samplers**

| Parameter | Number of Samples | max | mean | std dev | 3 sigma |
|---|---|---|---|---|---|
| pH | 191 | 9.49 | 6.55 | 0.81 | 8.82 |
| Conductivity (us/cm) | 191 | 382 | 48.61 | 54.65 | 212.57 |
| TSS (g/L) | 192 | 1.14 | 0.097 | 0.161 | 0.58 |
| TOSS (g/L) | 84 | 0.256 | 0.042 | 0.049 | 0.19 |
| Ca (mg/L) | 191 | 19.65 | 3.39 | 3.30 | 13.30 |
| Mg (mg/L) | 191 | 28 | 2.09 | 3.56 | 12.77 |
| K (mg/L) | 191 | 8.67 | 1.29 | 1.27 | 5.11 |
| TP (mg/L) | 191 | 3.35 | 0.26 | 0.40 | 1.46 |
| SRP (mg/L) | 191 | 1.76 | 0.11 | 0.25 | 0.85 |
| NH3-N(mg/L) | 191 | 1.7 | 0.12 | 0.25 | 0.88 |
| NO3 (mg/L) | 191 | 2.33 | 0.06 | 0.23 | 0.75 |
| TN (mg/L) | 191 | 7.79 | 1.16 | 1.29 | 5.02 |

**Table 5.3: Baseline (Pre-Harvest) Concentrations for Samples Collected from Hillslope Concentrations Samplers**

| Parameter | Number of Samples | max | mean | std dev | 3 sigma |
|---|---|---|---|---|---|
| pH | 130 | 8.77 | 6.0 | 0.48 | 7.23 |
| Conductivity (us/cm) | 130 | 432 | 40.16 | 45.21 | 175.80 |
| TSS (g/L) | 177 | 0.932 | 0.067 | 0.115 | 0.41 |
| TOSS (g/L) | 135 | 0.361 | 0.028 | 0.048 | 0.17 |
| Ca (mg/L) | 130 | 12.62 | 4.05 | 2.80 | 12.44 |
| Mg (mg/L) | 130 | 6.32 | 0.93 | 0.84 | 3.45 |
| K (mg/L) | 130 | 18.1 | 3.77 | 3.54 | 14.38 |
| TP (mg/L) | 130 | 2.22 | 0.38 | 0.36 | 1.45 |
| SRP (mg/L) | 130 | 1.49 | 0.23 | 0.27 | 1.04 |
| NH3-N(mg/L) | 130 | 3.59 | 0.39 | 0.68 | 2.42 |
| NO3 (mg/L) | 130 | 3.7 | 0.32 | 0.53 | 1.89 |
| TN (mg/L) | 130 | 10.04 | 1.90 | 1.57 | 6.61 |
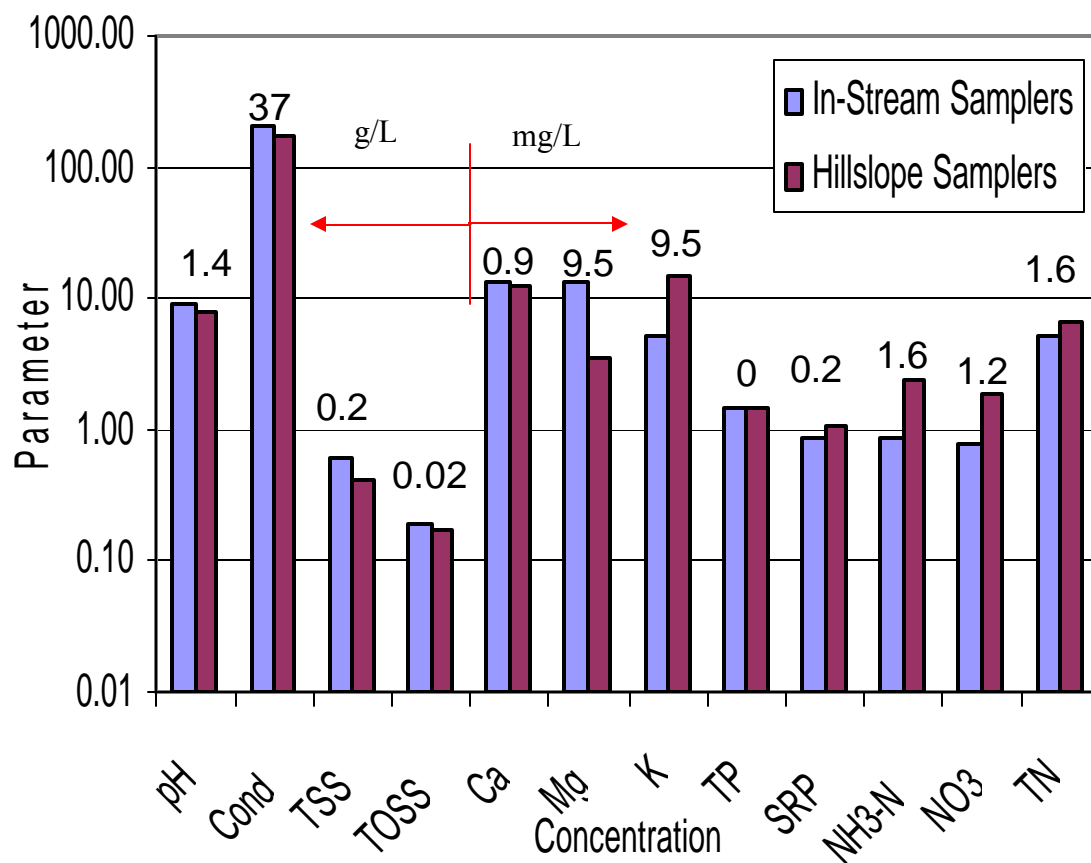
**Figure 5.2 Comparison in Baseline (Pre-Harvest) Concentrations for the 12 selected parameters from In-Stream and Hillslope Samplers the numbers above the columns represent the difference in the concentrations: October 2004 to January 2006**

The Ozark water samples were separated into those from the in-stream and those from the hillslope samples. The concentrations for the 12 water quality parameters are shown in Tables 5.2 and 5.3 for the in-stream and hillslope samplers respectively. The in-stream and hillslope concentrations are compared graphically in Figure 5.2. pH concentrations were slightly higher in in-stream than in hillslope samplers. A similar concentration increase is paralleled in the following concentrations: electrical conductivity, calcium, magnesium, and total suspended solids. The following hillslope sampler concentrations were found to be higher in hillslope samplers: total organic suspended solids, potassium, soluble reactive phosphorous, total nitrogen, nitrate, ammonia-nitrogen, and potassium. Total phosphorous was found to be equal in both sampling apparatuses.

Only two parameters had a substantial difference in concentrations with regard to sampling apparatus type: magnesium and potassium. The concentrations of magnesium were found to be 9.5 mg/L higher in in-stream than in hillslope samplers. Concentrations of potassium, however, were found to be 9.5 mg/L higher in hillslope than in in-stream samplers. Potassium is a soluble nutrient that is released in the decomposition of organic matter and higher in the sediment traps due to a non-diluted flow off of sediment traps. This was discussed more thoroughly in Chapter 4. Magnesium is a nutrient that is dominant in the geology of the Ozark sites. Settergren et al. 1972 found that a great deal of deep seepage occurred in the landscape of these surrounding areas. Due to this, the water seeping through the geology would weather the magnesium from the dolomite. It is interesting to note that although these concentrations vary the most, the electrical conductivity values for both sampling apparatuses are close (a difference of 37 us/cm).

This could be attributed to potassium being a cation and as such picked up in electrical conductivity readings.

## 5.4 Comparison of Water Samples Collected from Hillslope and In-Stream samplers with Grab samples

As previously explained in Chapter 4, 13 grab samples were collected. These concentrations were not included with the data presented in Table 5.2 and Table 5.3, but are included in Appendix 13.

**Table 5.4 Comparison of Grab Water Samples with Samples Collected from In-Stream and Hillslope Instrumentation**

| Parameter | Grab Sample mean (μ) | Grab Sample std dev (s) | Instrument mean μ | Instrument Baseline 3*s+μ |
|---|---|---|---|---|
| pH | 7.4 | 1.1 | 6.19 | 8.30 |
| EC (us/cm) | 124 | 70 | 45.33 | 199.61 |
| TSS (g/L) | 0.09 | 0.10 | 0.08 | 0.50 |
| TOSS (g/L) | 0.04 | 0.05 | 0.03 | 0.18 |
| Ca (mg/L) | 7.81 | 4.26 | 3.62 | 13.01 |
| Mg (mg/L) | 5.82 | 3.76 | 1.60 | 10.04 |
| K (mg/L) | 0.68 | 0.35 | 2.27 | 10.38 |
| TP (mg/L) | 0.08 | 0.11 | 0.26 | 1.30 |
| SRP (mg/L) | 0.01 | 0.01 | 0.16 | 1.08 |
| NH3-N (mg/L) | 0.05 | 0.08 | 0.22 | 1.67 |
| NO3 (mg/L) | 0.02 | 0.02 | 0.16 | 1.33 |
| TN (mg/L) | 1.23 | 1.50 | 1.43 | 5.80 |

A list of observations of the data is also included in Appendix 13. The observations of the data in Appendix 13 further reinforce the importance of seepage and geologic weathering as found by Settergren et al. 1972 to the concentrations of calcium and magnesium as well as the values of pH and electrical conductivity.

**5.5 Reasons for Reporting Concentrations from All Samples Collected out of Instrumentation**

In establishing the baseline (pre-harvest) concentrations for the water quality parameters, it was decided to composite all samples (in-stream and hillslope). This was considered an acceptable procedure since the concentrations calculated for the separated samples (Figure 5.2) were not substantially different (with the exceptions of magnesium and potassium concentrations). In addition to this, the full number of samples (384) would better illustrate the variation present in water samples that were collected from the study sites.

**5.6 Summary**

Due to seasonal trends of parameters as well as site variability in geology, hydrology, vegetation and precipitation events, the three sigma method was applied to all 12 selected parameters in order to establish baseline (pre-harvest) concentrations while accounting for the variation. The three sigma method encompasses 99.87 percent of all available water sample data. The baseline (pre-harvest) concentrations are concentrations are given below in Table 5.4. The concentrations in Figure 5.4 will be amended with additional measured data from additional sampling events prior to harvest of extended baseline data and the continued collection of data from the five control sites.

The baseline concentrations will be used to compare with post-harvest water quality parameters in order to assess whether or not the regenerative oak clear cut (ROCC) process, as practiced using the Missouri Department of Conservation's best management practices result in any change to those parameters. An example, hypothesized, comparison of pre- and post-harvest concentrations is shown in Figure 5.3

(Sheriff, 1997).  The water quality data in this thesis established the baseline (pre-harvest) concentrations.  There are two possible outcomes after the ROCC harvest (1) there will be an increase of concentrations for parameters, (2) there will be no increase of concentrations for parameters.

**Table 5.4 Background Concentrations for 12 Water Quality Parameters for the In-Stream and the Hillslope samplers**

| Parameter | Mean μ | Baseline Value (μ+3s) |
|---|---|---|
| pH | 6.19 | 8.3 |
| Conductivity (us/cm) | 45 | 199.61 |
| TSS (g/L) | 0.08 | 0.50 |
| TOSS (g/L) | 0.03 | 0.18 |
| Calcium (mg/L) | 3.62 | 13.01 |
| Mg (mg/L) | 1.6 | 10.04 |
| K (mg/L) | 2.27 | 10.38 |
| TP (mg/L) | 0.26 | 1.30 |
| SRP (mg/L) | 0.16 | 1.08 |
| NH3 (mg/L) | 0.22 | 1.67 |
| NO3 (mg/L) | 0.16 | 1.33 |
| TN (mg/L) | 1.43 | 5.80 |
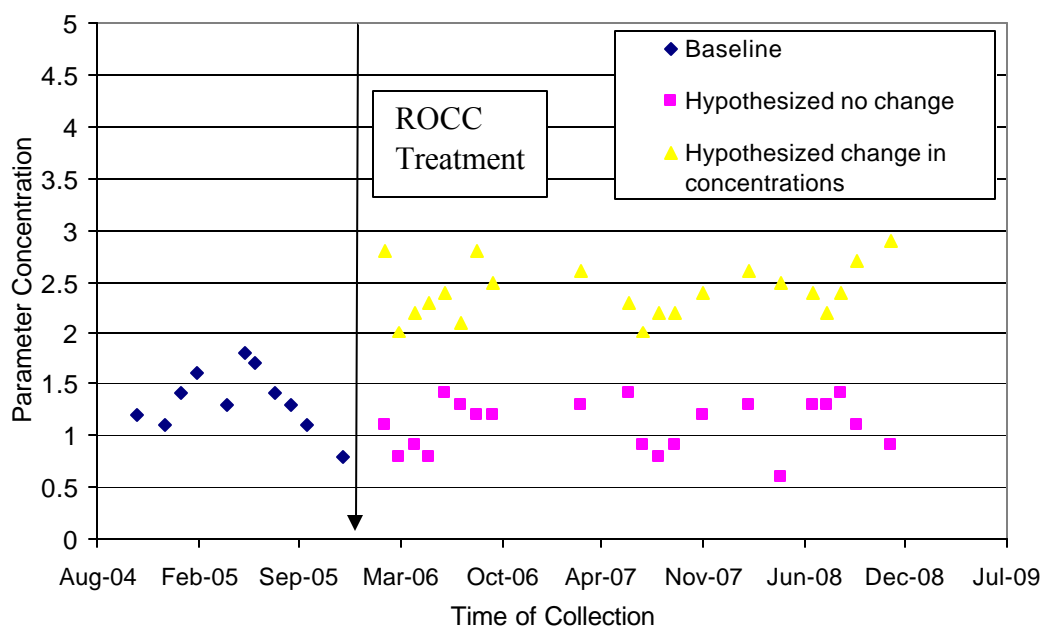


**Figure 5.3 Example of Pre - and Post-Harvest Comparison of Water Quality Parameters**

**Chapter 6 - Conclusions**

**6.1 Summary**

The Missouri Department of Conservation charged the Institute for Interdisciplinary Geotechnics of the University of Missouri with quantitatively assessing the effects of regenerative oak clear cuts, using MDC's best management practice, on the water quality in ephemeral drainage streams in the Missouri Ozarks. The best management practice consists of leaving a riparian buffer strip along streams of significant size. Judgment of the buffer is the responsibility of the local forester. The study encompasses fifteen sites located in Shannon and Reynolds counties. Ten of the sites are cut sites and five sites are control sites. There are two instrumentation regimes – "extensive" and "intensive". Intensive sites contain more instruments than extensive sites. Water samples are collected from instrumentation that is designed to capture surface flow. The water samples collected are analyzed for parameters that can indicate the affects of timber harvesting on water quality. The parameters include: pH, electrical conductivity, nitrate ($NO_3$), ammonia-nitrogen ($NH_3$-N), total nitrogen (TN), soluble reactive phosphorous (SRP), total phosphorous (TP), calcium (Ca), magnesium (Mg), potassium (K), total suspended solids (TSS), and total volatile suspended solids (TVSS).

The data presented in this thesis entails pre-harvest (baseline) water samples for the period – October 2004 to January 31, 2006. During this period, 384 samples were collected. The main objective of this thesis was to quantify pre-harvest (baseline) concentrations for the 12 water quality parameters. A secondary objective was to examine the data to better ascertain site parameters including geologic and hydraulic

processes as well as seasonal parameters to develop trends or correlations with the measured water quality. The baseline values were quantified using the three-sigma method which encapsulates 99.87 percent of the measured data for all parameters of interest.

## 6.2 Key Findings

Water samples were analyzed for 12 parameters. Methods were successfully selected to analyze all 12 parameters. The variations of concentrations with regard to season were evaluated. The data were also analyzed with regard to site variability, landform, site geology, and instrumentation type. The following key findings are based upon these analyses.

- Total phosphorous, soluble reactive phosphorous, potassium, calcium, magnesium, conductivity, pH, total nitrogen, nitrate, and ammonia-nitrogen were all found to reach peak concentrations in the May sampling event. This is thought to be correlated with degradation of detritus.

- Potassium, nitrate, total nitrogen, ammonia-nitrogen, were found to be elevated in hillslope samplers relative to the amount of these parameters found in in-stream bottle samplers. The higher concentrations were found to coincide with degradation of leaf matter.

- pH was found to be lower in the hillslope samplers than in the in-stream samples. This finding reinforces the hypothesis that degradation of organic matter in the hillslope samplers is the reason for the higher nutrient releases in the hillslope samples.

- Concentrations for: Total phosphorous, soluble reactive phosphorous, calcium, magnesium, conductivity, total suspended solids and total volatile solids did not vary with instrumentation method.

- Although total suspended solid magnitudes were not found to vary with instrumentation type, amounts of total suspended solids were found to relate to where the samples were collected in the landscape such as slope percent or the stream length upstream of in-stream sampler.

- A baseline value for each of the 12 parameters was established.  The values were based on more than one year of water sampling events, and were established so that less than 13/10,000 will be greater than the established background value. The background concentrations for the 12 water quality parameters are given all in Table 6.1.

**Table 6.1 Background concentrations for 12 Selected Water Quality Parameters for Composited In-Stream and Hillslope Samples (2004 – 2006)**

| Parameter | Max | Min | Mean | Background ($\mu + 3s$) |
|---|---|---|---|---|
| pH | 9.49 | 4.90 | 6.12 | 8.3 |
| Conductivity (us/cm) | 432.00 | 4.16 | 45.33 | 199.61 |
| TSS (g/L) | 1.14 | 0.00 | 0.08 | 0.50 |
| TOSS (g/L) | 0.36 | 0.00 | 0.03 | 0.18 |
| Ca (mg/L) | 19.65 | 0.04 | 3.62 | 13.01 |
| Mg (mg/L) | 28.00 | 0.01 | 1.60 | 10.04 |
| K (mg/L) | 18.10 | 0.00 | 2.27 | 10.38 |
| TP (mg/L) | 3.35 | 0.00 | 0.28 | 1.30 |
| SRP (mg/L) | 1.99 | 0.00 | 0.17 | 1.08 |
| $NH_3$-N(mg/L) | 3.59 | 0.00 | 0.22 | 1.67 |
| $NO_3$ (mg/L) | 3.70 | 0.00 | 0.16 | 1.33 |
| TN (mg/L) | 10.04 | 0.01 | 1.43 | 5.80 |

**Chapter 7 - Recommendations**

**7.1 Introduction**

Determining the effect of timber harvesting on water quality is a complex and expansive task. It includes site selection, field instrumentation, laboratory water analyses, and evaluation of the water quality in light of geographic vegetation, climatic and timber management practices. Recommendations are listed in the following sections to improve all facets of the project. A listing of ways to improve laboratory testing is given in Section 7.2. Suggestions to improve the other facets of the project are listed in Section 7.3. Section 7.4 is a summary.

**7.2 Laboratory Testing Recommendations**

A comprehensive laboratory testing program is underway. The current program emphasizes high level quality control; however, following are items which would improve the laboratory analyses.

- Total organic carbon (TOC) as well as dissolved organic carbon (DOC) should be analyzed. Carbon is an important nutrient in the growth of and sustaining of the forest ecosystem. Carbon is also a factor in providing an energy source for aquatic based organisms.

- Background samples were not analyzed in duplicate. This should be done on all future analyses to enhance quality assurance.

- Water samples should be analyzed for iron and aluminum. These two constituents are dominant in the soils in and around the study area. A measure of these constituents after harvest might indicate mass wasting events that include soils below the A-horizon.

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- Water samples should be analyzed for carbonic acid. Carbonic acid is formed from the degradation of leaf litter and other organic debris and is also formed from interaction of carbonate rocks – limestone and dolomite. By analyzing for carbonic acid a better indicator of rock weathering and thus stream alterations of the hydrological properties of the ephemeral drainage way could be explored.

## 7.3 Project Recommendations

The goal of the overall project is to quantitatively document the effect of regenerative oak clear cutting on water quality in ephemeral drainage ways in the Ozarks. The following recommendations would improve the overall objective of the project.

- Water samples are collected from two types of instrumentation, in-stream and hillslope samplers. The instrumentation is located on a myriad of varying landscape and stream hydrological formations. By grouping data from similar formations, one could better determine the effect of such landscape attributes on water quality in ephemeral drainage ways. The following attributes have been analyzed by Mueller (2006): site area, relief, stream gradient, drainage density, slope, geology, bifurcation ratio. Spatial distribution of soil morphological properties should be correlated with concentrations measured for the 12 parameters.

- It has been discussed within this thesis that the amount of detritus and the time of its degradation play an important role in the measured water quality parameters. Timber harvesting might remove the source of the litter layer, a tree's crown, which provided the detritus in hillslope samplers. As such the measured concentrations for post-harvest might be skewed.

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**7.4 Summary**

  The Missouri Department of Conservation timber harvest project is a project came about due to concerned about the impacts of silvicultural practices on the surrounding watershed.  The recommendations made with regard to laboratory practices and the overall project should help to improve the project and further enhance our understanding of our natural resource.

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# LIST OF APPENDICES

Appendix 1

## Procedure for determining Ammonia-Nitrate

*Adapted from:*
Methods for the Chemical Evaluation of Waste Water. MCWW[3] 351.2. Salicylate
Method. And changed with regard to Hach Method 8155.

## Introduction
In solution, ammonia combines with chlorine to form monochloramine which then reacts
with salicylate to form 5-amoinosalicylate. This chemical is oxidized by sodium
nitroprusside to form a blue color which is masked by the yellow color of excess reagent
to form a green color which is then analyzed colorimetrically by the Spectron 20D+.

## Chemicals

Ammonia Cyanurate Powder Pillows. . . cat no. 26531-99
Ammonia Salicylate Powder Pillows. . . cat no. 26532-99
Ammonium Chloride

## Operating Notes:

1.  All glassware and sample holders must be cleaned by a sulfuric acid bath
2.  Refrigerate samples at $4^oC$ until they are run. If they will not be run within 24
    hours, add 5 drops of 100% sulfuric acid per 100 ml. Usually we freeze samples
    so the sample must be totally thawed out before the sample for analyses can be
    poured. Freezing of samples has been shown to minimize degradation for years if
    needed.
3.  Use DI water or better for the preparation of stocks, standards, and reagents.
4.  Operate colorimeter using a 655 nm filter. Set machine to red filter.
5.  If color is present analyze sample before the addition of reagents to establish a
    baseline reading and then after. The difference between the two readings is the
    reading that must be used for the amount of nitrogen that is present. Set the
    spectrophotometer to absorbance mode. After both pillows are added decant
    mixed sample into another vial. This is to prevent the particles from getting
    sucked into the sampling tube.
6.  1.572 g of ammonia chloride are needed to make 0.4 g/L NH3-N
7.  Add 10 mls of sample and add the salicylate pillow first and then add the
    cyarurate pillow a few minutes later. Wait 20 minutes for analyzing.

Appendix 2

## **Procedure for Determining Total Suspended Solids (TSS)**

*Adapted From*:
2540 C.  Total Solids Dried at 180°C Standard Methods for the Examination of Water
and Wastewater, 1992

Introduction
In this procedure, solids are collected from samples by filtering the sample through a
glass fiber filter and then dried.

## **Materials**

A 1000 ml vacuum flask
A glass fiber filter of 0.45 μm pore size
An oven capable of temperature above 100°C
A holding container for the filter

## **Operating Notes:**

1.  The filters must be washed, dried and then weighed.  Washing includes either (1)
    holding the filter with tongs and then washing the filter with DI water (2) floating the
    filters in a container with DI water.

2.  The sample that will be filtered must be completely thawed out.  To enhance thawing
    a hot water bath can be used.

3.  Pour 100 ml of sample through filter.

4.  Place the filter in the holding container

5.  Pour the filtrate into the "dissolved" plastic container (60 ml Nalgene bottle)

6.  Wash all parts of the filtering apparatus with DI water three times

7.  Every five samples use a filter blank

Appendix 3

## **Procedure for Fixed and Volatile Solids Ignited at 500°C (TVSS)**

*Adapted From*:
2540 E. Fixed and Volatile Solids Ignited at 500°C Standard Methods for the
Examination of Water and Wastewater, 1992

Introduction
In this procedure, filters are burned at 500°C in order to ascertain the amount of volatile
and fixed samples are in the collected sample.

## **Materials**

A glass fiber filter of 0.45 um pore size
An oven capable of temperature above 500°C
A holding container for the filter
A balance capable of 0.0000 g

## **Operating Notes:**

1. Place filter and holder into blast furnace at 500°C

2. Leave overnight

3. Re-weigh

Appendix 4

## **Procedure for determining Nitrate and Total Nitrogen after alkaline persulfate digestion**

*Adapted from:*
APHA 1992. 4500-NO3 E. Cadmium Reduction method in Standard Methods for the Examination of Water and Wastewater 18th edition. American Public Health Association. 1992. Also utilizing Hach method 8192 (Powder pillows)

Introduction
In this procedure nitrate is reduced to nitrite in the presence of cadmium. The nitrite produced is determined by diazotizing with sulfanilamide and coupling with N-(1-napthyl)-ethylenediamine dihydrochloride to form a highly colored dye that is measured.

## **Chemicals**

NitraVer 6 Nitrate Powder Pillows. . . cat no. 21072-49
NitraVer 3 Nitrite Powder Pillows. . . cat no. 21071-69
Potassium nitrate for standards

## **Operating Notes:**

1       All glassware and sample holders must be cleaned by a sulfuric acid bath
2       Refrigerate samples at 4$^o$C until they are run. If they will not be run within 24 hours, add 5 drops of 100% sulfuric acid per 100 ml. Usually we freeze samples so the sample must be totally thawed out before the sample for analyses can be poured. Freezing of samples has been shown to minimize degradation for years if needed.
3       Use DI water or better for the preparation of stocks, standards, and reagents.
4       Operate colorimeter using a 543 nm filter. Set machine to white filter.
5       If color is present analyze sample before the addition of reagents to establish a baseline reading and then after. The difference between the two readings is the reading that must be used for the amount of nitrogen that is present. Set the spectrophotometer to absorbance mode.
6       Potassium nitrate is used for standards. To make a 800 mg/L standard, use 1.305 g of potassium nitrate
7       Pour 10 mls out of sample container. Add Nitrate pillows wait a few minutes then add nitrite pillows and wait for 20 minutes

Appendix 5

## **Procedure for determining Dissolved Phosphorous or Total Phosphorous following alkaline persulfate digestion**

*Adapted from:*
APHA 1992. 4500-P E. Ascorbic Acid Method in Standard Methods for the Examination of Water and Wastewater 18th edition. American Public Health Association. 1992.

Introduction
In this procedure phosphate reacts with ammonium molybdate and potassium antimonyl tartrate to form antimony-phosphomolybdate complex, which reacts with ascorbic acid to form a blue colored solution whose color is proportional to the initial phosphorous concentration of the sample.

## **Chemicals (ACS grade or equivalent)**

Potassium antimonyl tartrate
Ammonium molybdate
Ascorbic acid
Sulfuric Acid
Potassium phosphate monobasic anhydrous (standards)

## **Operating Notes:**

1. All glassware and sample holders must be cleaned by a sulfuric acid bath
2. Refrigerate samples at 4$^o$C until they are run. If they will not be run within 24 hours, add 5 drops of 100% sulfuric acid per 100 ml. Usually we freeze samples so the sample must be totally thawed out before the sample for analyses can be poured. Freezing of samples has been shown to minimize degradation for years if needed.
3. Use DI water or better for the preparation of stocks, standards, and reagents.
4. Operate colorimeter using a 650 nm filter. Set machine to red filter.
5. Use potassium phosphate for standards. For 300 mg/L of phosphate use 1.321g of potassium phosphate. Dilute to reach standards that are in range of sample concentrations. A 1 mg/L, a 0.1 mg/L and a 0.02 mg/L standard is made.
6. If color is present analyze sample before the addition of reagents to establish a baseline reading and then after. The difference between the two readings is the reading that must be used for the amount of phosphate that is present. Set the spectrophotometer to absorbance mode.
7. Take 10 mls from sample container add mixed reagent and wait for 20 minutes

## Preparation of Reagents

Dilute Sulfuric Acid

|  | 1L |
|---|---|
| Concentrated Sulfuric Acid | 140 ml |
| DI water | 860 ml |

Initially place DI water into volumetric flask; slowly add concentrated sulfuric acid to water while stirring.  Allow to cool and store in room temperature or refrigerator.  Good for about 1 year.

### Potassium antimonyl tartrate solution

For 100 ml: add 0.3g Potassium antimonyl tartrate (same as antimonyl potassium tartrate) to approximately 50 ml DI water.  Dissolve and dilute to 100 ml.  Store refrigerated.  The solution is stable for three months.  Proportionately adjust mixture for varying volumes.

### Ammonium molybdate solution

For 100 ml:  Add 4g ammonium molybdate to approximately 50 ml DI water.  Dissolve and dilute to 100 ml.  Store refrigerated.  The solution is stable for three months. Proportionately adjust mixture for varying volumes.

### Ascorbic acid solution

For 100 ml:  Add 1.76g ascorbic acid to approximately 50 ml DI water.  Dissolve and dilute to 100 ml.  Store refrigerated.  The solution is stable for about 1 month. Proportionately adjust mixture for varying volumes.

### Combined Reagent

For 100 ml:  Add in order; 50 ml Dilute Sulfuric acid, 5 ml potassium antimonyl tartrate solution, 15 ml ammonium molybdate solution and 30 ml ascorbic acid solution.  Mix well by swirling after adding each solution.  Mix fresh daily.

1.  Each tray should have a blank at the beginning, followed by a high standard and two other lower standards.  The end of the tray should have a Hach standard.  Although the Hach standard reads 1 mg/L PO4, since we are testing for phosphate the concentration is really 0.326 mg/L.

Appendix 6

## **Potassium Persulfate Digestion for use before Analyzing Total Phosphorous and Total Nitrogen**

Potassium persulfate digestion, method APHA Method 4500-N C, is required for digestion of total phosphorous and total nitrogen.  The samples are digested together as outlined by Ebina, Tsutsui, and Shirai (1983).  This technique of digestion oxidizes all nitrogenous compounds to nitrate at $100^{o}C$.  The method is important  for phosphorous because phosphorous may occur in combination with organic matter; and, digestion releases the phosphorous in its orthophosphate form

Mix 20.5 g of potassium persulfate and 3.0 g of sodium hydroxide in 1000 ml of DI water
Mixture takes a long time to mix therefore a sonicator can assist in mixing the solution
A daily mixture must be made to properly digest the sample

Mix 10 ml of sample with 2.2 ml of digestion mixture

The mixture is placed in an autoclave for 30 minutes at 98 – 137 kPa.

Standards must be analyzed with each batch of samples digested.  The standards analyzed will be of equal concentrations that are analyzed for the dissolved nutrients – nitrate and soluble reactive phosphorous.

A glutamic acid standard will be analyzed for digestion quality -

Digestion tape is used to verify proper digestion conditions in the autoclave

Appendix 7

**Results of the Degradation Study Carried Out for Four Days.  Two solutions were made and then analyzed for degradation of nutrients**
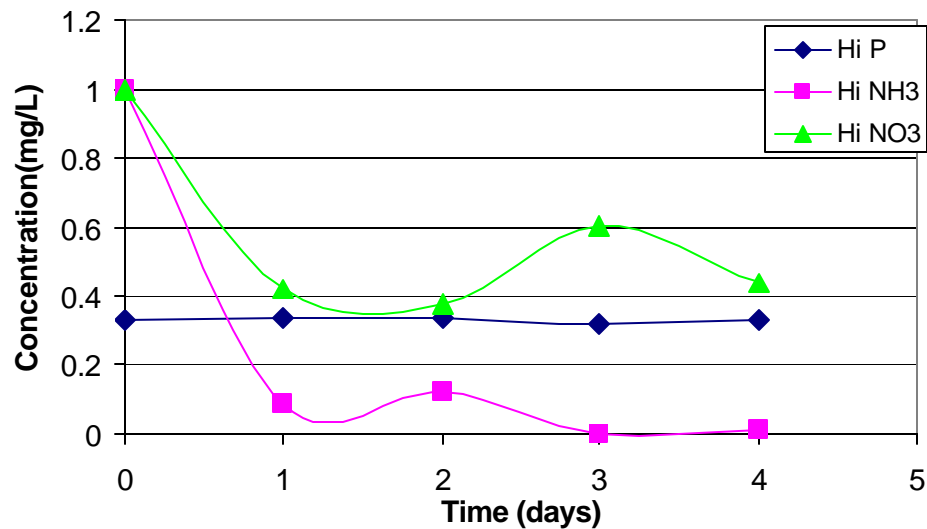


**Figure 1:  Nutrient Concentrations versus Storage Time in Dictating the Degradation Rate for Nutrients Sampled from the High Concentration Samples**
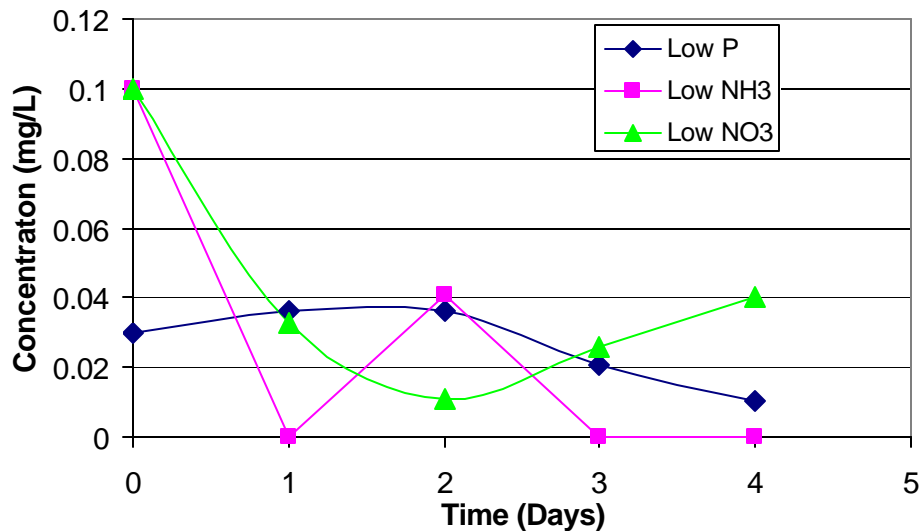


**Figure 2:  Nutrient Concentrations versus Storage Time in Dictating the Degradation Rate for Nutrients Sampled from the Low Concentration Samples**

Appendix 8

**The Results of a Comparison Study – the AA-Technicon at Columbia
Environmental Research Center versus the Spectron 20D+ at the Soil
Characterization Lab**

**Table 1:  Salicylate Method Comparison (NH$_3$) results from machine
comparison study**

| | Sample | | Spectron20D+ Conc (ppm) | Technicon Conc (ppm) | % Recovery |
|---|---|---|---|---|---|
| 12/14/2004 | CR7-5B | WS1-0 | 0.12 | 0.12 | 100 |
| 1/10/2005 | CR7-6 | WS5-0 | 0.03 | 0.03 | 100 |
| 1/10/2005 | CR7-2 | SD4 | 0.17 | 0.17 | 100 |
| 1/10/2005 | CR7-6 | WS6-0 | 0.01 | 0.01 | 100 |
| 1/10/2005 | CR7-5C | SD3 | 0.31 | 0.35 | 88 |
| 1/19/2005 | CR11-9 | WS1-0 | 0 | 0 | 100 |
| 1/19/2005 | CR11-9 | WS3-0 | 0 | 0 | 100 |
| 1/19/2005 | A34-2 | WS3-0 | 0.03 | 0.03 | 100 |
| 1/19/2005 | CR7-5C | SD4 | 0.32 | 0.37 | 86 |
| 1/19/2005 | CR7-6 | SD4 | 0.03 | 0.03 | 100 |
| 1/19/2005 | CR11-1 | WS2-0 | 0.06 | 0.06 | 100 |
| 1/19/2005 | CR11-1 | WS3-0 | 0.03 | 0.03 | 100 |
| 1/19/2005 | CR11-3 | WS3-3 | 1.52 | 1.55 | 98 |
| 1/19/2005 | CR7-6 | WS5-0 | 0.03 | 0.03 | 100 |
| 1/19/2005 | CR11-3 | WS3-6 | 0 | 0 | 100 |
| 1/19/2005 | CR7-6 | WS4-0 | 0.02 | 0.02 | 100 |
| 2/15/2005 | A34-1 | WS7-0 | 0.06 | 0.06 | 100 |
| 2/15/2005 | A34-1 | WS10-0 | 0.04 | 0.04 | 100 |
| 2/15/2005 | A34-1 | WS7-0 | 0.06 | 0.06 | 100 |
| 2/15/2005 | A34-1 | WS5-3 | 0.13 | 0.13 | 100 |
| 2/18/2005 | CR7-6 | WS5-0 | 0.03 | 0.03 | 100 |
| 2/18/2005 | CR7-5C | SD4 | 0.36 | 0.36 | 100 |

Appendix 9

**Table 2: Cadmium Reduction Method ($NO_3$, TN) results for machine comparison study**

|  | Sample |  | Spectron20D+ Conc. (ppm) | Technicon Conc (ppm) | % Recovery |
|---|---|---|---|---|---|
| 12/14/2004 | CR7-5B | WS1-0 | 0.02 | 0.02 | 100.00 |
| 1/10/2005 | CR7-6 | WS5-0 | 0 | 0 | 100.00 |
| 1/10/2005 | CR7-2 | SD4 | 2.16 | 2.13 | 98 |
| 1/10/2005 | CR7-6 | WS6-0 | 0.01 | 0.01 | 100.00 |
| 1/10/2005 | CR7-5C | SD3 | 0.01 | 0.01 | 100.00 |
| 1/19/2005 | CR11-9 | WS1-0 | 0.13 | 0.13 | 100.00 |
| 1/19/2005 | CR11-9 | WS3-0 | 2.31 | 2.33 | 99 |
| 1/19/2005 | A34-2 | WS3-0 | 0.03 | 0.03 | 100.00 |
| 1/19/2005 | CR7-5C | SD4 | 0.04 | 0.04 | 100.00 |
| 1/19/2005 | CR7-6 | SD4 | 0.68 | 0.65 | 95 |
| 1/19/2005 | CR11-1 | WS2-0 | 0.01 | 0.01 | 100.00 |
| 1/19/2005 | CR11-1 | WS3-0 | 0.01 | 0.01 | 100.00 |
| 1/19/2005 | CR11-3 | WS3-3 | 0 | 0 | 100.00 |
| 1/19/2005 | CR7-6 | WS5-0 | 0.01 | 0.01 | 100.00 |
| 1/19/2005 | CR11-3 | WS3-6 | 0.18 | 0.21 | 85 |
| 1/19/2005 | CR7-6 | WS4-0 | 0.02 | 0.02 | 100.00 |
| 2/15/2005 | A34-1 | WS7-0 | 0 | 0 | 100.00 |
| 2/15/2005 | A34-1 | WS10-0 | 1.82 | 1.85 | 98 |
| 2/15/2005 | A34-1 | WS7-0 | 0 | 0 | 100.00 |
| 2/15/2005 | A34-1 | WS5-3 | 0.03 | 0.03 | 100.00 |
| 2/18/2005 | CR7-6 | WS5-0 | 0.02 | 0.02 | 100.00 |
| 2/18/2005 | CR7-5C | SD4 | 0.04 | 0.04 | 100.00 |

Appendix 10

**Table 3: Ascorbic Acid Method (SRP, TP) results for machine comparison study**

| | Sample | | Spectron20D+ Conc (ppm) | Technicon Conc (ppm) | % Recovery |
|---|---|---|---|---|---|
| 12/14/2004 | CR7-5B | WS1-0 | 0.08 | 0.07 | 88 |
| 1/10/2005 | CR7-6 | WS5-0 | 0.04 | 0.04 | 100 |
| 1/10/2005 | CR7-2 | SD4 | 0.31 | 0.3 | 96 |
| 1/10/2005 | CR7-6 | WS6-0 | 0.04 | 0.04 | 100 |
| 1/10/2005 | CR7-5C | SD3 | 0 | 0 | 100 |
| 1/19/2005 | CR11-9 | WS1-0 | 0.01 | 0.01 | 100 |
| 1/19/2005 | CR11-9 | WS3-0 | 0.07 | 0.06 | 85 |
| 1/19/2005 | A34-2 | WS3-0 | 0.02 | 0.02 | 100 |
| 1/19/2005 | CR7-5C | SD4 | 0.1 | 0.1 | 100 |
| 1/19/2005 | CR7-6 | SD4 | 0.1 | 0.08 | 80 |
| 1/19/2005 | CR11-1 | WS2-0 | 0.03 | 0.03 | 100 |
| 1/19/2005 | CR11-1 | WS3-0 | 0.07 | 0.05 | 83 |
| 1/19/2005 | CR11-3 | WS3-3 | 1.1 | 1.3 | 85 |
| 1/19/2005 | CR7-6 | WS5-0 | 0.05 | 0.05 | 100 |
| 1/19/2005 | CR11-3 | WS3-6 | 0.1 | 0.1 | 100 |
| 1/19/2005 | CR7-6 | WS4-0 | 0.06 | 0.05 | 83 |
| 2/15/2005 | A34-1 | WS7-0 | 0.01 | 0.01 | 100 |
| 2/15/2005 | A34-1 | WS10-0 | 0.02 | 0.02 | 100 |
| 2/15/2005 | A34-1 | WS7-0 | 0.01 | 0.01 | 100 |
| 2/15/2005 | A34-1 | WS5-3 | 0.02 | 0.02 | 100 |
| 2/18/2005 | CR7-6 | WS5-0 | 0.08 | 0.08 | 100 |
| 2/18/2005 | CR7-5C | SD4 | 0.08 | 0.09 | 89 |

Appendix 11

**Detection Limits for Technicon (Carried Out by Ben Lakish at USGS-Columbia Environmental Research Center)**

Introduction

The Instrument Detection Limit (IDL) is defined as mean noise (average of all blanks) plus 3 times the standard deviation of a low standard (0.025*high standard in the first run, 0.01*high standard in the second two runs).  High standards were 1mg/l NH3 as N, 1mg/l NO3 as N and 200 ug/l P.

Calculated Instrument Detection Limit for NH3 on the Technicon: 3 runs yielded 3 standard deviations: 0.005774 (n=4), 0.003536 (n=8), 0.004629 (n=8).  Average standard deviation =0.004646.  3* average standard deviation= 0.013938. Average blank (n=55) for the 3 runs was 0.002449 mg/l N.  Instrument Detection Limit (IDL) estimated as 0.016387 mg/l.

Standard deviations for a low standard of soluble reactive phosphorus (SRP) were 1.050448 (n=8), 0.339997 (n=8) and 0.913845 (n=8), average standard deviation for the three runs was 0.768097, average blank (n=55) was -0.89291 standard deviation for all blanks was 1.645663.  Average blank was changed to positive 0.89291 for this calculation.  IDL is estimated as 3.1972 ug/L P.

Standard deviations for a low standard of nitrate +nitrite (NO3+NO2) were 0.0046291 (n=8), 0 (n=8) and 0.005345 (n=8) average standard deviation for the three runs was 0.003324775.  Average of all blanks (n=55) was 0.005454545 standard deviation of all blanks was 0.005025.  The estimated IDL for NO3 is 0.015429 mg/l as N.

Similar Studies were performed on the Spectron 20D+ and the following was discovered.

- Total Phosphorous has an IDL of 0.09 mg/L

- Soluble Reactive Phosphorous has an IDL of 0.008 mg/L

- Total Nitrogen has an IDL of 0.009 mg/L

- Nitrate has an IDL of 0.008 mg/L

- Ammonia-Nitrogen has an IDL of 0.011 mg/L

Appendix 12

## **The Number of Observations each Concentration Occurred for the 12 Parameters**

## **Tested in the Ozark Study**



n = 384
μ = 0.08 g/L
s = 0.14
μ+3s = 0.5 g/L
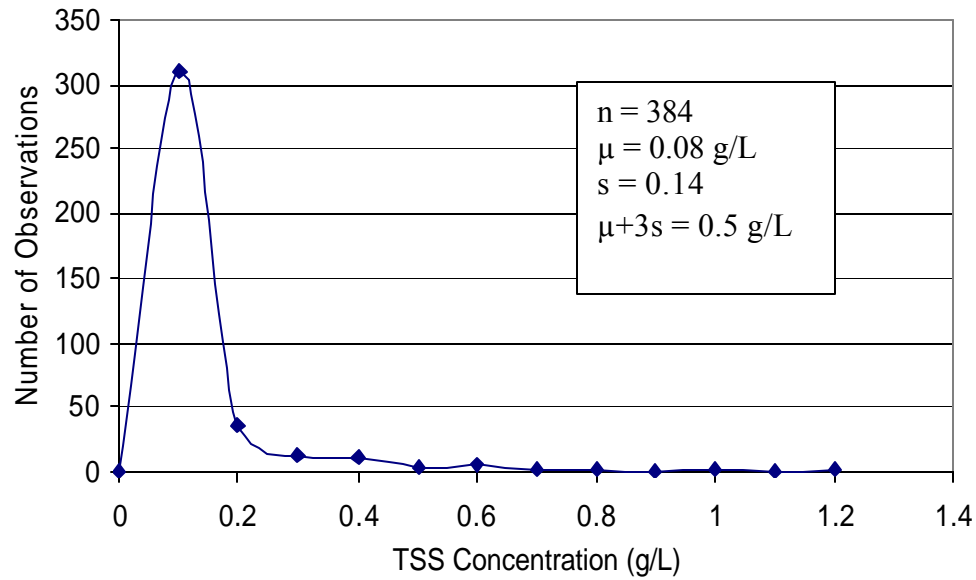
**Figure 1:  The Distribution Plot of TSS collected for all samples out of In-Stream Samplers and Hillslope samplers**



n = 280
μ = 0.03 g/L
s = 0.05
μ+3s = 0.18 g/L
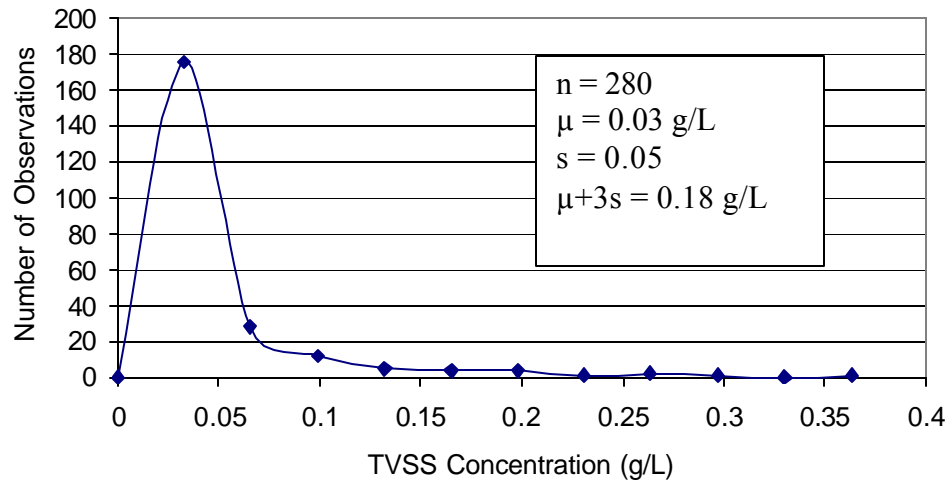
**Figure 2:  The Distribution Plot of TVSS collected for all samples out of In-Stream Samplers and Hillslope samplers**
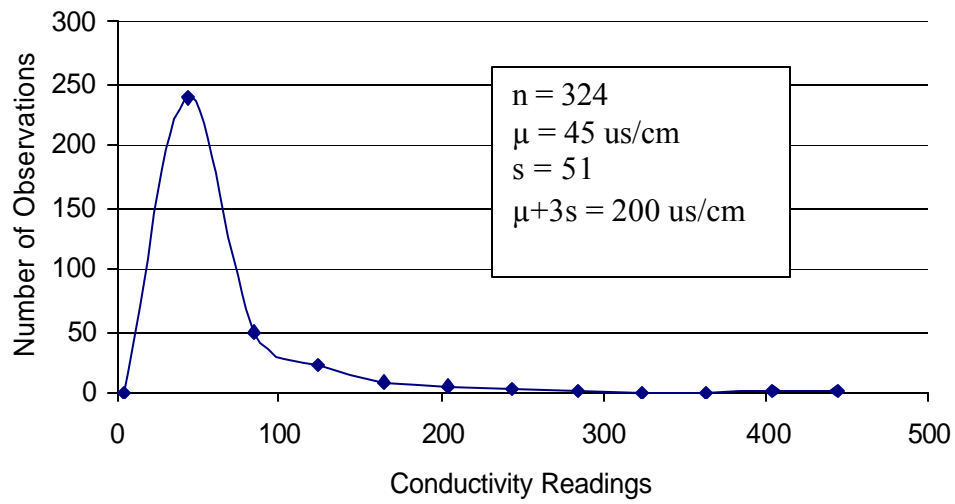
**Figure 3: The Distribution of Electrical Conductivity for all Samples Collected out of In-Stream Samplers and Hillslope samplers**
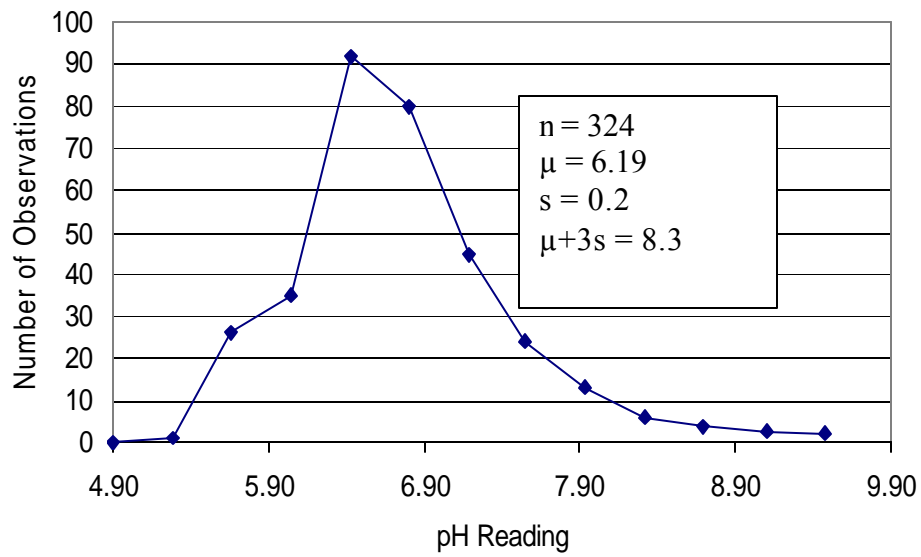


**Figure 4: The Distribution of pH for all Samples Collected out of In-Stream Samplers and Hillslope samplers**
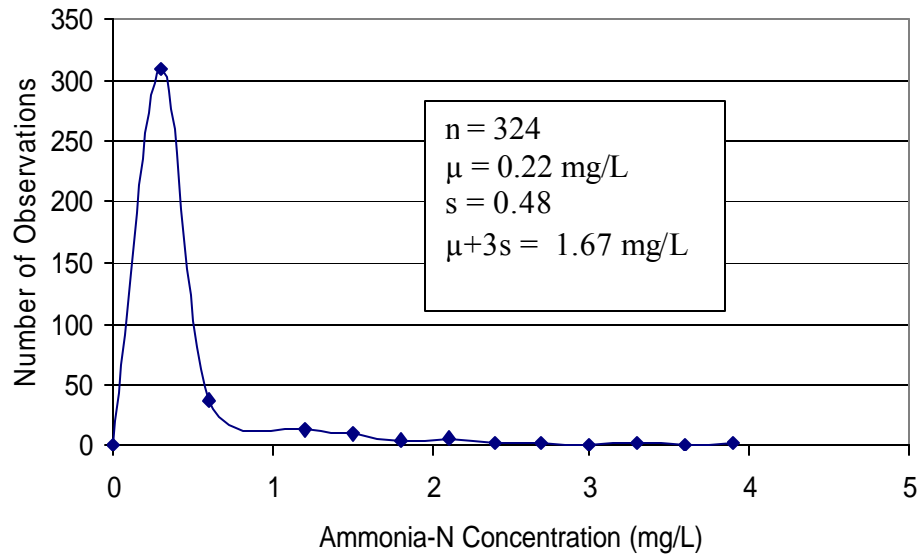
**Figure 5:  The Distribution of Ammonia-Nitrogen for all Samples Collected out of In-Stream Samplers and  Hillslope samplers**
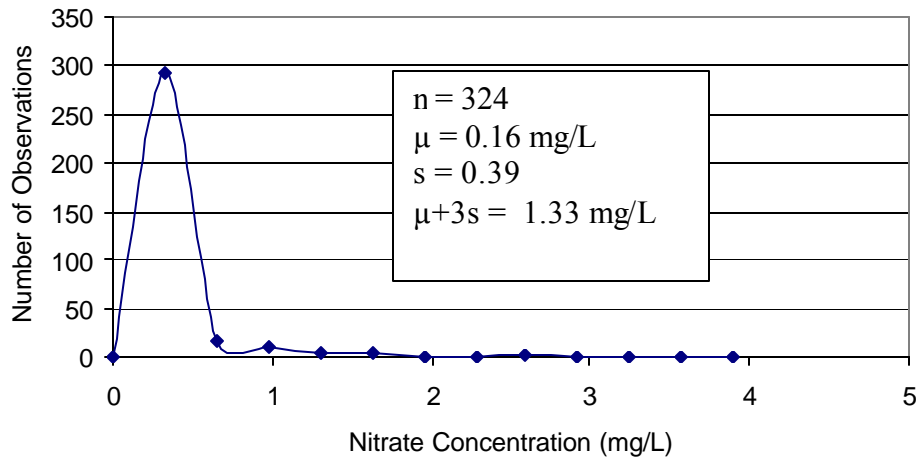


**Figure 6:  The Distribution of Nitrate for all Samples Collected out of In-Stream Samplers and Hillslope samplers**
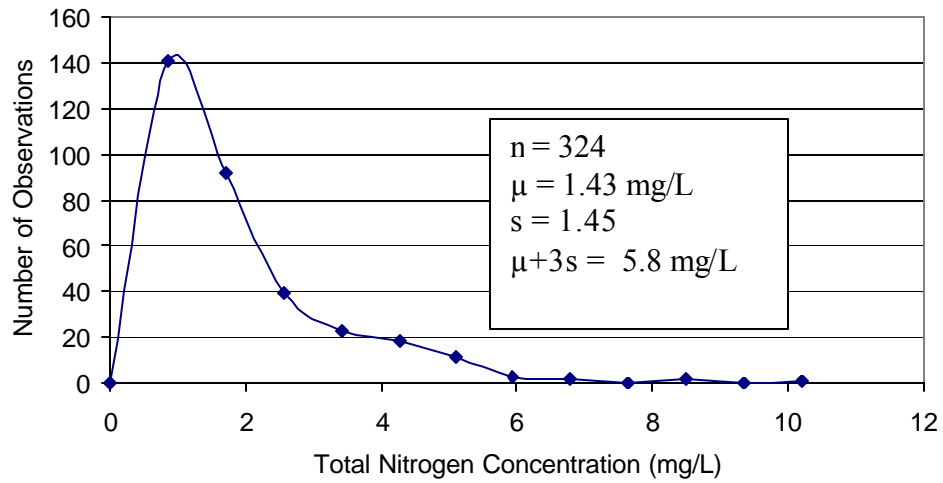
**Figure 7:  The Distribution of Total Nitrogen for all Samples Collected out of In-Stream Samplers and Hillslope samplers**
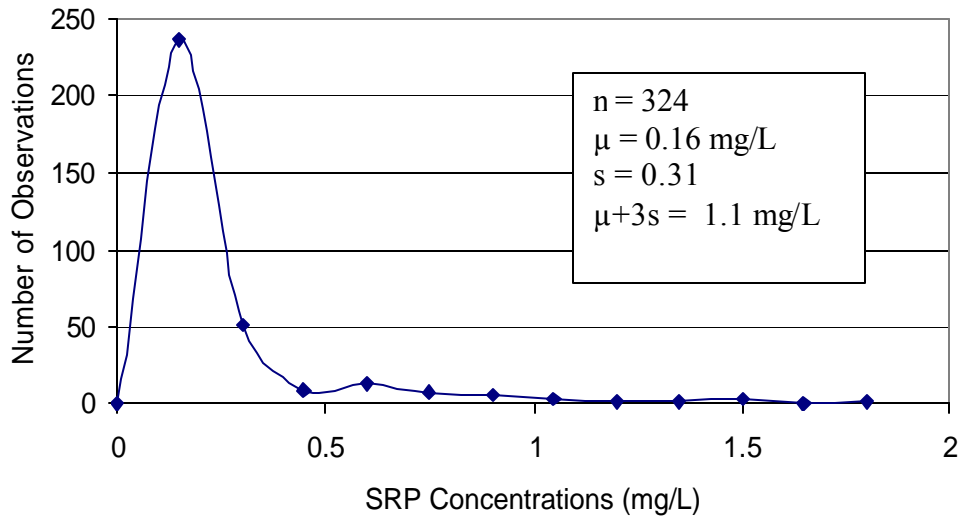


**Figure 8:  The Distribution of Soluble Reactive Phosphorous for all Samples Collected out of In-Stream Samplers and Hillslope samplers**
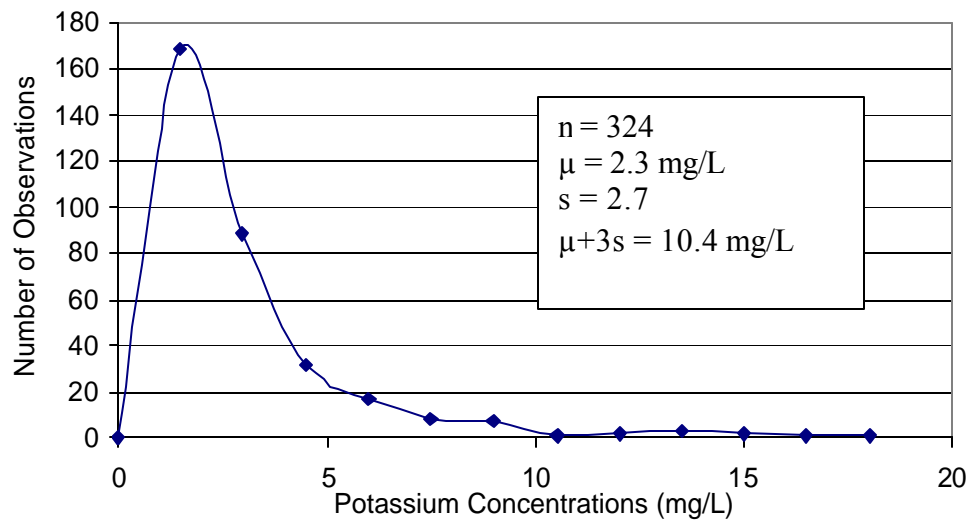
**Figure 9:  The Distribution of Potassium for all Samples Collected out of In-Stream Samplers and Hillslope samplers**
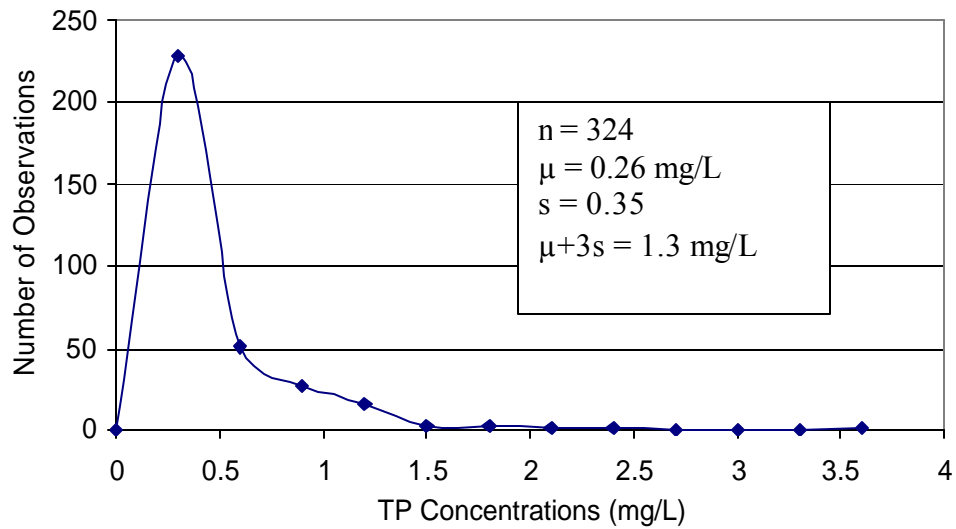


**Figure 10:  The Distribution of Total Phosphorous for all Samples Collected out of In-Stream Samplers and Hillslope samplers**

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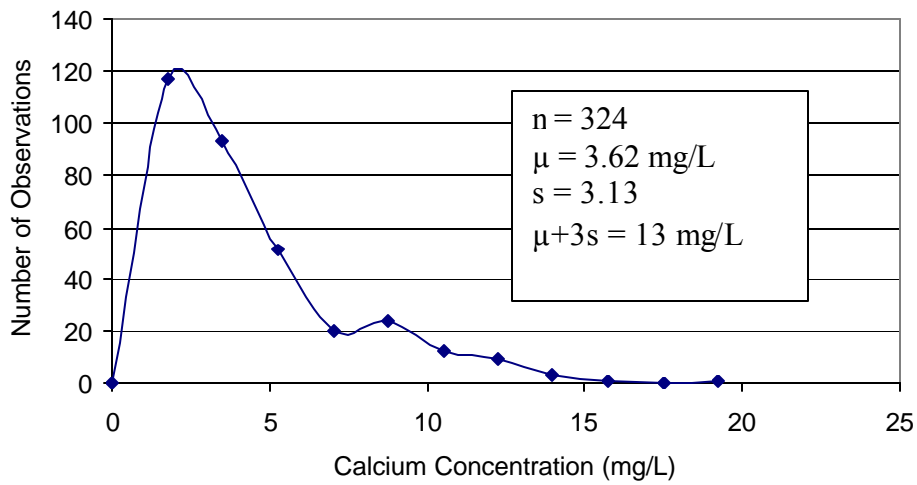
**Figure 11:  The Distribution of Calcium for all Samples Collected out of In-Stream Samplers and Hillslope samplers**
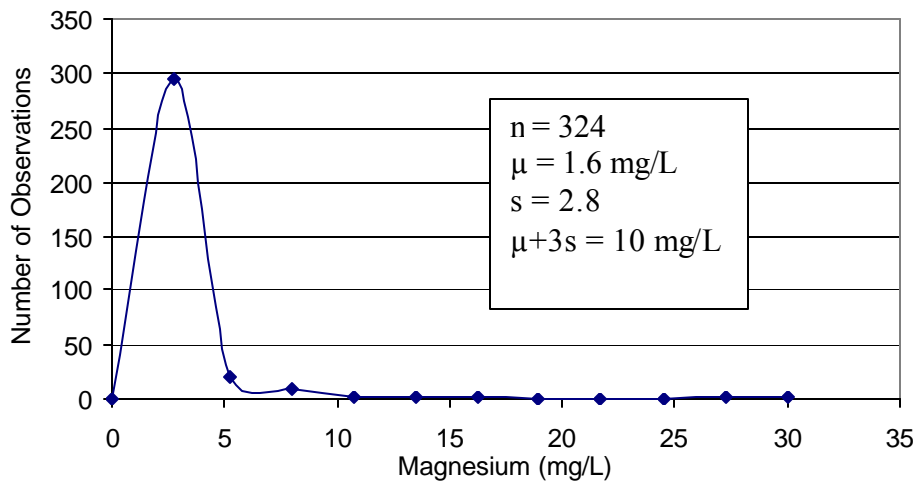


**Figure 12:  The Distribution of Magnesium for all Samples Collected out of In-Stream Samplers and Hillslope samplers**

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Appendix 13

A total of 13 grab samples were collected in addition to the 384 samples collected from the in-stream and hillslope instrumentation.

**Table 13.1 Raw Data Collected from Grab Samples from all Sampling Events**

| Date | Area | Site | | (us/cm) | g/L | | (mg/L) | | | | | | | |
|------|------|------|----|----|-----|------|----|----|----|----|----|------|-----|----|
| | | | pH | EC | TSS | TOSS | Ca | Mg | K | TP | SRP | NH$_3$-N | NO$_3$ | TN |
| 2/05 | Spring | A27-2 | 8.52 | 135.1 | 0.35 | | 7.8 | 2.7 | 0.28 | 0.4 | 0.01 | 0.12 | 0.01 | 0.18 |
| 1/05 | In-stream | A34-1 | 6.46 | 36.8 | 0.034 | | 2.2 | 2 | 0.26 | 0.02 | 0 | 0.01 | 0.02 | 0.23 |
| 2/05 | Turn-out | A34-1 | 6.93 | 31.4 | 0.19 | | 2.1 | 2.4 | 0.32 | 0.04 | 0.01 | 0.05 | 0 | 0.06 |
| 11/05 | River | CR - 106 | 9.08 | 135.1 | 0.101 | 0.026 | 10.66 | 9.83 | 1.42 | 0.05 | 0.03 | 0.06 | 0.03 | 3.47 |
| 11/05 | in-stream | CR11-3 | 6.63 | 31 | 0.183 | 0.156 | 3.43 | 1.47 | 1.05 | 0.13 | 0.04 | 0.01 | 0 | 0.81 |
| 11/05 | Out of 2nd order | CR7 - 2 | 9.17 | 93.6 | 0.027 | 0.014 | 5.61 | 6.42 | 0.78 | 0.04 | 0.01 | 0.04 | 0 | 2.69 |
| 12/04 | 3rd Order | CR7-2 | 7.36 | 244 | 0.002 | | 17.7 | 6.2 | 0.77 | 0.01 | 0 | 0.02 | 0.02 | 0.04 |
| 4/05 | Spring | A25-3 | 7.55 | 223 | 0.02 | | 5.7 | 15.2 | 0.38 | 0.05 | 0 | 0 | 0 | 3.26 |
| 2/05 | Spring | A34-2 | 7.78 | 196.1 | 0.037 | | 11.4 | 4.2 | 0.41 | 0.24 | 0.02 | 0.28 | 0.02 | 0.38 |
| 11/05 | River | CR - 106 (2) | 8.27 | 169.9 | 0.035 | 0.023 | 7.72 | 4.49 | 0.58 | 0.03 | 0.03 | 0.03 | 0.05 | 3.91 |
| 11/05 | River | Current River @ 106 Bridge | 9.49 | 108 | 0.084 | 0.025 | 8.86 | 7.5 | 0.89 | 0.02 | 0.02 | 0.01 | 0.03 | 0.26 |
| 11/05 | Before 3rd order | CR7-2 | 7.25 | 85 | 0.016 | 0.014 | 10.07 | 7.55 | 1 | 0.03 | 0.01 | 0.02 | 0.03 | 0.14 |
| 11/05 | After 3rd order | Shop Hollow 2 | 7.09 | 127.5 | 0.146 | 0.033 | 8.33 | 5.66 | 0.69 | 0.01 | 0.01 | 0.02 | 0.06 | 0.51 |

1. The three River samples collected in November 2005 have the following concentrations higher than the means concentrations collected out of the hillslope and in-stream samplers: pH mean of 8.9, EC of 140 us/cm, calcium a mean of 9.1 mg/L, magnesium a mean of 7.5 mg/L, total nitrogen with a mean of 2.6 mg/L. The remaining

parameters were very close to the mean concentrations collected out of the hillslope and in-stream samplers.

2. Site CR7-2 is the only site that intersects a 3$^{rd}$ order intermittent stream. Four samples were collected from the junction of the instrumented stream and the intermittent stream. The pH average of the four samples was 7.7 the corresponding EC mean value was 138 us/cm. Mean calcium and magnesium concentrations, 10.4 and 6.5 mg/L respectively, also exceeded those mean concentrations collected out of the in-stream and hillslope instrumentation. No variation in TSS, TVSS was found and the remaining parameters were found to be close to the mean concentrations from the in-stream and hillslope samplers.

3. Three samples were collected at the exits of observable springs. The following parameters were found to exceed the mean concentrations found in the water samples collected from the instrumentation: pH with a mean value 8, EC with a mean value of 190 us/cm, calcium with a mean concentration of 8.3 mg/L and magnesium with a concentration of 7.4 mg/L.

## Appendix 14 Results of Aluminum and Iron on Samples Collected from the May Sampling Event

| Total of 30 Samples/All Sed | Samples from 5/18/05 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Concentration (ppm) | | | | | | | | | |
| SAMPLE | Ca | Mg | K | Al (ICP) | Al (AA) | Fe (ICP) | Fe (AA) | Mn (ICP) | TSS (g/l) | Color |
| CR7-5C SD5 | 1.3 | 0.7 | 8.4 | 0.029 | 0 | 0.002 | 0 | 0.223 | 0.09 | Brown |
| CR7-6 SD3 | 3.5 | 1 | 3.92 | 0.009 | 0 | 0 | 0 | 0.073 | 0.028 | Brown |
| CR7-5C SD2 | 13.5 | 1.4 | 7.51 | 0.035 | 0 | 0 | 0 | 0.406 | 0.012 | Yellow |
| CR7-5B SD3 | 2.9 | 0.9 | 2.76 | 0.007 | 0 | 0 | 0 | 0.027 | 0.022 | Clear |
| CR7-2 SD4 | 5 | 12.5 | 1.02 | 0.001 | 0 | 0 | 0 | 0.003 | 0.018 | Yellow |
| CR7-2 SD3 | 3.2 | 1.9 | 15.96 | 0.009 | 0 | 0.004 | 0 | 0.682 | 0.05 | Brown |
| CR11-9 WS1-0 | 5.2 | 7.8 | 3.88 | 0.005 | 0 | 0 | 0 | 0.008 | 0.1 | Green |
| CR11-1 SD5 | 14 | 0.8 | 6.12 | 0.051 | 0 | 0.012 | 0 | 0.378 | 0.018 | Yellow |
| CR11-1 SD3 | 3.2 | 1.2 | 7.96 | 0.027 | 0 | 0 | 0 | 0.062 | 0.009 | Clear |
| CR11-1 SD1 | 5.3 | 0.7 | 3.58 | 0.017 | 0 | 0.001 | 0 | 0.249 | 0.028 | Brown |
| A34-2 WS6-0 | 1 | 4 | 2.01 | 0.033 | 0 | 0.016 | 0 | 0.01 | 0.043 | Yellow |
| A34-2 WS4-0 | 4.7 | 0.9 | 1.48 | 0.052 | 0 | 0.007 | 0 | 0.022 | 0.132 | Yellow |
| A34-2 SD5 | 5.6 | 1.8 | 6.97 | 0.015 | 0 | 0.016 | 0 | 0.391 | 0.016 | Brown |
| A34-2 SD4 | 1.1 | 1.7 | 10.59 | 0.021 | 0 | 0.058 | 0 | 0.889 | 0.224 | Yellow |
| A34-1 WS3-0 | 4.3 | 0.9 | 0.42 | 0.058 | 0 | 0.004 | 0 | 0.011 | 0.009 | Yellow |
| A34-1 SD3 | 5.4 | 0.9 | 13.02 | 0.024 | 0 | 0.015 | 0 | 0.195 | 0.036 | Brown |
| A34-1 SD1 | 2.7 | 1.8 | 6.03 | 0.021 | 0 | 0.016 | 0 | 0.254 | 0.086 | Yellow |
| A27-2 SD2 | 0.4 | 0.1 | 0.1 | 0.005 | 0 | 0 | 0 | 0.248 | 0.019 | Brown |
| A27-1 WS7-0 | 7.7 | 16 | 6.4 | 0.013 | 0 | 0.006 | 0 | 0.196 | 0.013 | Yellow |
| A27-1 WS6-0 | 5.2 | 23 | 1.07 | 0.004 | 0 | 0 | 0 | 0.001 | 0.02 | Yellow |
| A27-1 WS3-0 | 6 | 1 | 5.32 | 0.015 | 0 | 0.011 | 0 | 0.008 | 0.362 | Brown |
| A27-1 SD3 | 11.5 | 1 | 0.47 | 0.032 | 0 | 0.035 | 0 | 0.394 | 0.023 | Brown |
| A25-3 SD3 | 11.6 | 1.8 | 0.39 | 0.034 | 0 | 0 | 0 | 0.006 | 0.037 | Brown |
| A25-2 WS1-0 | 7.6 | 1.1 | 11.95 | 0.001 | 0 | 0.006 | 0 | 0.018 | 0.038 | Yellow |
| A25-2 SD5 | 8.3 | 1 | 12.78 | 0.008 | 0 | 0.021 | 0 | 0.226 | 0.036 | Brown |
| A25-2 SD1 | 6 | 1 | 10.13 | 0.027 | 0 | 0.009 | 0 | 0.166 | 0.042 | Brown |
| A17-2 SD1 | 4 | 0.8 | 5.93 | 0.038 | 0 | 0 | 0 | 0.31 | 0.031 | Clear |
| A17-1 SD1 | 7.8 | 1 | 11.81 | 0.013 | 0 | 0.022 | 0 | 0.434 | 0.027 | Brown |
| | | | | | | | | | | |
| Abe Smith-MDC Timber Harvest | 5/18/05-Sample Summary | | | | | | | | | |

Appendix 15: October 2004 Sampling Event

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N(mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CR11-3 | WS1 | 0 | 6.56 | 52.43 | 0.07 | | 7.6 | 0.9 | 3.19 | 0.02 | 0.02 | 0 | 0.08 | 0.75 |
| CR7-5C | SD3 | | 6.12 | 70.8 | 0.11 | | 9.3 | 0.4 | 3.29 | 0.01 | 0.01 | 0.03 | 0.05 | 1.02 |
| CR11-3 | WS1 | 0 | 6.42 | 49.8 | 0.05 | | 8.5 | 0.9 | 3.46 | 0.45 | 0.45 | 1.02 | 0.07 | 1.1 |

Appendix 16: December 2004 Sampling Event

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N(mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CR11-1 | WS4 | 0 | 7.39 | 16.3 | 0.012 | | 1.1 | 0.5 | 0.76 | 0.23 | 0.01 | 0.03 | 0.02 | 1.68 |
| CR11-1 | WS5 | 0 | 7.35 | 34.4 | 0.009 | | 2.3 | 0.4 | 0.93 | 0.02 | 0.01 | 0.17 | 0.04 | 0.45 |
| CR11-3 | WS1 | 0 | 7.03 | 38 | 0.094 | | 3.2 | 1.6 | 1.99 | 0.01 | 0.01 | 0.02 | 0.02 | 0.82 |
| CR11-3 | WS3 | 0 | 7.25 | 170.3 | 0.026 | | 0.7 | 0.3 | 0.41 | 0.61 | 0.03 | 0.08 | 0.04 | 2.98 |
| CR7-2 | WS1 | 0 | 8 | 120.1 | 0.11 | | 8.4 | 5.2 | 1.03 | 0.04 | 0.01 | 0.02 | 0.02 | 1.07 |
| CR7-2 | GRAB | | 7.36 | 244 | 0.002 | | 17.7 | 6.2 | 0.77 | 0.01 | 0.00 | 0.02 | 0.02 | 0.04 |
| CR7-5B | WS1 | 0 | 6.32 | 23.1 | 0.014 | | 0.7 | 0.4 | 0.44 | 0.04 | 0.04 | 0.12 | 0.02 | 2.34 |
| CR7-5C | SD5 | | 6.65 | 32.4 | 0.046 | | 2.5 | 0.5 | 6.41 | 0.17 | 0.04 | 0.02 | 0.04 | 0.47 |
| CR7-6 | WS2 | 0 | 7.74 | 12.11 | 0.014 | | 0.5 | 0.2 | 2.55 | 0.04 | 0.02 | 0.02 | 0.02 | 0.84 |

Appendix 17: The First Sampling Event in January 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N(mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A27-2 | WS3 | 0 | 5.47 | 18.22 | 0.025 | | 1 | 0.8 | 1.28 | 0.09 | 0.08 | 0.29 | 0 | 1.17 |
| A34-1 | WS4 | 0 | 6.72 | 26.7 | 0.047 | | 1.4 | 1.4 | 0.37 | 0.02 | 0.02 | 0.02 | 0.01 | 0.04 |
| A34-1 | WS6 | 0 | 6.22 | 14.45 | 0.022 | | 0.7 | 0.6 | 0.24 | 0.03 | 0.02 | 0.01 | 0 | 0.1 |
| A34-1 | WS7 | 0 | 6.88 | 28.8 | 0.009 | | 1.7 | 0.9 | 1.46 | 0.05 | 0.01 | 0.01 | 0.69 | 1.09 |
| A34-1 | WS7 | 3 | 7.34 | 22.5 | 0.09 | | 1.2 | 1.2 | 0.28 | 0.03 | 0.02 | 0.02 | 0.01 | 0.5 |
| A34-1 | WS7 | 6 | 7.21 | 25.2 | 0.068 | | 1.1 | 1.1 | 0.49 | 0.02 | 0.02 | 0.01 | 0.01 | 0.21 |
| A34-1 | WS8 | 0 | 6.84 | 27 | 0.019 | | 1.4 | 1.6 | 0.28 | 0.02 | 0.02 | 0 | 0.03 | 0.53 |
| A34-1 | WS8 | 3 | 7 | 26.4 | 0.028 | | 1.2 | 1.3 | 0.3 | 0.02 | 0.01 | 0 | 0.01 | 0.04 |
| A34-1 | WS8 | 6 | 7.19 | 25 | 0.015 | | 1.2 | 1.4 | 0.28 | 0.02 | 0.02 | 0.01 | 0.02 | 0.06 |
| A34-1 | WS9 | 0 | 6.83 | 24.2 | 0.021 | | 1.8 | 1.1 | 0.35 | 0.03 | 0.01 | 0.09 | 0.02 | 0.11 |
| A34-1 | WS10 | 0 | 6.54 | 19.7 | 0.073 | | 1 | 0.8 | 0.41 | 0.04 | 0.02 | 0.03 | 0.03 | 0.08 |
| A34-1 | GRAB | | 6.46 | 36.8 | 0.034 | | 2.2 | 2 | 0.26 | 0.02 | 0.00 | 0.01 | 0.02 | 0.23 |
| A34-2 | WS2 | 0 | 6.08 | 22.3 | 0.03 | | 1.7 | 0.9 | 0.38 | 0.01 | 0.01 | 0.01 | 0.11 | 0.86 |
| CR11-1 | WS2 | 0 | 7.09 | 36.3 | 0.031 | | 1.1 | 0.8 | 3.97 | 0.57 | 0.06 | 0.01 | 0 | 1.2 |
| CR11-1 | WS5 | 0 | 7.41 | 17.26 | 0.015 | | 0.9 | 0.7 | 0.35 | 0.09 | 0.08 | 0.01 | 0.01 | 0.17 |
| CR11-3 | WS3 | 0 | 6.73 | 34.1 | 0.021 | | 2.2 | 1.9 | 0.28 | 0.01 | 0.01 | 0.03 | 0 | 0.16 |
| CR11-9 | WS1 | 0 | 7.49 | 160.1 | 0.008 | | 9.3 | 7.2 | 2.78 | 0.03 | 0.02 | 0.04 | 0.05 | 0.11 |
| CR7-2 | WS1 | 0 | 7.12 | 99.3 | 0.081 | | 3.3 | 5.8 | 0.31 | 0.02 | 0.02 | 0.01 | 0.01 | 0.12 |
| CR7-2 | SD4 | | 7.12 | 91.6 | 0.178 | | 10.5 | 0.7 | 0.26 | 0.31 | 0.30 | 0.02 | 2.13 | 2.16 |
| CR7-5C | SD3 | | 7.56 | 4.16 | 0.044 | | 0.1 | 0.1 | 0 | 0.09 | 0.08 | 0.01 | 0.01 | 3.87 |
| CR7-6 | WS5 | 0 | 7.5 | 17.87 | 0.073 | | 1.4 | 0.7 | 0.22 | 0.03 | 0.03 | 0.01 | 0 | 1.09 |
| CR7-6 | WS6 | 0 | 7.2 | 57.1 | 0.042 | | 3.5 | 3.3 | 1.62 | 0.02 | 0.02 | 0 | 0.01 | 0.09 |
| CR7-6 | WS6 | 3 | 7.85 | 44.4 | 0.007 | | 2.4 | 2.7 | 0.59 | 0.20 | 0.09 | 0.01 | 0.01 | 0.1 |
| CR7-6 | WS6 | 6 | 7.31 | 44.8 | 0.031 | | 3.1 | 2.9 | 0.37 | 0.07 | 0.01 | 0 | 0.02 | 0.11 |
| CR7-6 | WS8 | 0 | 7.84 | 236 | 0.135 | | 7.1 | 13.2 | 0.22 | 0.04 | 0.00 | 0.01 | 0 | 0.25 |

Appendix 18: The Second Sampling Trip in January 2005 (1 of 2)

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N(mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A17-2 | WS1 | 0 | 6.83 | 45.5 | 0.067 | | 2.1 | 1.1 | 0.38 | 0.26 | 0.01 | 0.01 | 0.01 | 0.03 |
| A17-2 | WS2 | 0 | 6.37 | 16.87 | 0.032 | | 1.4 | 0.6 | 0.52 | 0.01 | 0.01 | 0.01 | 0.01 | 0.05 |
| A25-2 | SD3 | | 6.49 | 26.5 | 0.051 | | 2.4 | 0.4 | 1.39 | 0.06 | 0.05 | 0.79 | 0.03 | 0.85 |
| A34-1 | WS1 | 0 | 5.51 | 20.7 | 0.023 | | 3 | 0.7 | 1.05 | 0.56 | 0.01 | 0 | 0.4 | 0.06 |
| A34-1 | WS4 | 0 | 6.22 | 10.82 | 0.009 | | 0.8 | 0.4 | 0.15 | 0.01 | 0.00 | 0 | 0.01 | 1.48 |
| A34-1 | WS6 | 0 | 5.43 | 10.32 | 0.022 | | 0.8 | 0.6 | 0.23 | 0.25 | 0.00 | 0 | 0.04 | 0.3 |
| A34-1 | WS7 | 0 | 6.72 | 33.4 | 0.046 | | 1.2 | 1.1 | 0.38 | 0.37 | 0.00 | 0 | 0.01 | 0.33 |
| A34-1 | WS7 | 3 | 6.56 | 23.1 | 0.015 | | 2.6 | 1.2 | 0.35 | 0.27 | 0.00 | 0 | 0.02 | 0.07 |
| A34-1 | WS7 | 6 | 6.37 | 21.4 | 0.01 | | 1.1 | 1.1 | 0.23 | 0.38 | 0.00 | 0 | 0.02 | 4.92 |
| A34-1 | WS8 | 0 | 6.67 | 21.9 | 0.036 | | 1.5 | 1.2 | 0.39 | 0.26 | 0.00 | 0 | 0.01 | 0.13 |
| A34-1 | WS8 | 3 | 6.96 | 27.6 | 0.032 | | 1.2 | 1.3 | 0.34 | 0.02 | 0.01 | 0.01 | 0.01 | 0.47 |
| A34-1 | WS8 | 6 | 6.57 | 22.3 | 0.014 | | 1.1 | 1.2 | 0.3 | 0.01 | 0.01 | 0.01 | 0.01 | 0.11 |
| A34-1 | WS9 | 0 | 6.91 | 39.1 | 0.52 | | 1.7 | 1.2 | 0.51 | 0.01 | 0.00 | 0 | 0.01 | 0.26 |
| A34-1 | WS9 | 3 | 6.52 | 22.3 | 0.067 | | 2.8 | 1.4 | 0.97 | 0.01 | 0.00 | 0.03 | 0.01 | 0.21 |
| A34-1 | WS10 | 0 | 6.37 | 16.87 | 0.071 | | 1.2 | 0.7 | 0.24 | 0.01 | 0.01 | 0 | 0.02 | 1.1 |
| A34-1 | WS10 | 6 | 6.45 | 17.92 | 0.028 | | 2 | 1.8 | 0.22 | 0.17 | 0.00 | 0 | 0.02 | 3.66 |
| A34-2 | WS2 | 0 | 6.09 | 20.7 | 0.095 | | 1.4 | 0.6 | 0.41 | 0.28 | 0.02 | 0.02 | 0.06 | 0.13 |
| A34-2 | WS3 | 0 | 6.06 | 18.9 | 0.101 | | 2.4 | 0.7 | 0.3 | 0.02 | 0.02 | 0.03 | 0.03 | 0.03 |
| A34-2 | WS4 | 0 | 5.48 | 20.2 | 0.041 | | 0.7 | 0.9 | 0.63 | 0.15 | 0.03 | 0.09 | 0.01 | 0.06 |
| A34-2 | WS4 | 6 | 6.76 | 24.1 | 0.028 | | 1.5 | 0.6 | 0.21 | 0.01 | 0.01 | 0.01 | 0.02 | 0.13 |
| A34-2 | WS5 | 0 | 8.93 | 87.1 | 0.043 | | 5 | 5.2 | 0.86 | 0.01 | 0.01 | 0 | 0.01 | 0.1 |
| A34-2 | WS6 | 0 | 6.82 | 76.4 | 0.067 | | 4.1 | 5 | 0.31 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 |
| A34-2 | WS6 | 3 | 8.62 | 68.6 | 0.037 | | 5 | 4.8 | 0.47 | 0.01 | 0.01 | 0 | 0.02 | 0.21 |

Appendix 18 (continued): The Second Sampling Trip in January 2005 (2 of 2)

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N (mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CR11-1 | WS2 | 0 | 6.52 | 18.55 | 0.03 | | 1.2 | 0.7 | 0.5 | 0.12 | 0.03 | 0.06 | 0.01 | 0.2 |
| CR11-1 | WS3 | 0 | 6.03 | 6.94 | 0.04 | | 0.4 | 0.3 | 0.12 | 0.03 | 0.03 | 0.03 | 0.01 | 0.09 |
| CR11-1 | WS4 | 0 | 7.2 | 17.55 | 0.039 | | 1 | 0.7 | 0.44 | 0.03 | 0.03 | 0.02 | 0 | 0.15 |
| CR11-1 | WS5 | 0 | 6.33 | 14.15 | 0.295 | | 0.8 | 0.5 | 0.43 | 0.13 | 0.13 | 0.13 | 0.01 | 0.42 |
| CR11-3 | WS1 | 0 | 6.89 | 26 | 0.142 | | 2.2 | 1.2 | 0.82 | 0.08 | 0.02 | 0 | 0 | 0.02 |
| CR11-3 | WS2 | 0 | 7.23 | 9.96 | 0.016 | | 1.2 | 0.5 | 0.03 | 0.22 | 0.22 | 0.02 | 0.01 | 4.26 |
| CR11-3 | WS3 | 0 | 6.82 | 27.5 | 0.14 | | 1.7 | 1.4 | 0.27 | 0.07 | 0.03 | 0.05 | 0 | 5.04 |
| CR11-3 | WS3 | 3 | 7.11 | 43.1 | 0.059 | | 2.2 | 1.3 | 2.57 | 1.56 | 1.37 | 1.55 | 0.18 | 1.82 |
| CR11-3 | WS3 | 6 | 6.83 | 20.1 | 0.047 | | 2 | 1.2 | 0.9 | 0.21 | 0.14 | 0 | 0.21 | 1.95 |
| CR11-9 | WS1 | 0 | 7.56 | 53.9 | 0.018 | | 1.3 | 0.9 | 0.48 | 0.32 | 0.01 | 0.11 | 0.13 | 0.62 |
| CR11-9 | WS1 | 3 | 8.52 | 109.5 | 0.082 | | 8 | 4.8 | 3.16 | 0.29 | 0.01 | 0 | 0.02 | 1.01 |
| CR11-9 | WS3 | 0 | 7.12 | 21.1 | 0.047 | | 1.2 | 1 | 0.88 | 0.06 | 0.05 | 0.1 | 2.33 | 6.5 |
| CR7-2 | WS3 | 0 | 6.32 | 17.53 | 0.016 | | 1.3 | 0.4 | 0.64 | 1.17 | 0.02 | 0.06 | 0.01 | 1.46 |
| CR7-2 | WS3 | 3 | 7.62 | 69.6 | 0.169 | | 5.2 | 1.1 | 8.67 | 1.01 | 0.72 | 0.28 | 0 | 1.32 |
| CR7-2 | WS6 | 0 | 6.73 | 127.3 | 0.032 | | 5.2 | 1.6 | 0.53 | 0.09 | 0.03 | 0.06 | 0.01 | 0.42 |
| CR7-2 | WS6 | 6 | 7.11 | 46.5 | 0.042 | | 2.7 | 2.7 | 0.55 | 0.23 | 0.06 | 0.01 | 0.01 | 0.56 |
| CR7-5B | WS1 | 0 | 6.41 | 18.04 | 0.063 | | 1.3 | 0.6 | 0.75 | 0.12 | 0.05 | 0.03 | 0.02 | 0.25 |
| CR7-5B | WS3 | 0 | 6.11 | 16.6 | 0.098 | | 1.2 | 0.5 | 0.93 | 0.05 | 0.04 | 0.09 | 0.01 | 0.25 |
| CR7-5B | WS4 | 0 | 6.7 | 11.72 | 0.114 | | 0.9 | 0.3 | 0.33 | 0.13 | 0.10 | 0.06 | 0.01 | 0.08 |
| CR7-5B | WS4 | 3 | 6.33 | 18.11 | 0.059 | | 1.5 | 0.6 | 0.88 | 0.06 | 0.05 | 0.03 | 0.04 | 2.41 |
| CR7-5C | WS1 | 0 | 6.66 | 5.78 | 0.302 | | 0.6 | 0.2 | 0.05 | 0.16 | 0.01 | 0.03 | 0.01 | 2.48 |
| CR7-5C | WS5 | 0 | 6.82 | 17.72 | 0.091 | | 1.3 | 0.7 | 0.61 | 0.14 | 0.05 | 0.03 | 0.02 | 2.75 |
| CR7-5C | WS5 | 3 | 6.78 | 17.95 | 0.045 | | 1.2 | 0.6 | 0.66 | 0.06 | 0.00 | 0.05 | 0.02 | 0.16 |
| CR7-5C | SD4 | | 5.83 | 23.8 | 0.052 | | 0.8 | 0.3 | 1.5 | 0.03 | 0.09 | 0.37 | 0.22 | 0.58 |
| CR7-6 | WS4 | 0 | 5.6 | 13.32 | 0.023 | | 0.6 | 0.4 | 0.84 | 0.28 | 0.04 | 0.02 | 0.02 | 0.93 |
| CR7-6 | WS5 | 0 | 5.9 | 12.62 | 0.256 | | 0.8 | 0.5 | 0.33 | 0.34 | 0.05 | 0.03 | 0.01 | 0.56 |
| CR7-6 | SD4 | | 6.92 | 118 | 0.186 | | 12 | 2.3 | 4.26 | 0.03 | 0.08 | 0.03 | 0.65 | 0.69 |
| CR7-2 | WS1 | 0 | 7.84 | 62.4 | 0.254 | | 7.5 | 9.2 | 0.47 | 0.01 | 0.01 | 0.01 | 0.1 | 0.35 |

Appendix 19: February Sampling Trip 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N(mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A17-1 | WS3 | 0 | 5.91 | 15.66 | 0.026 | | 1.7 | 0.7 | 0.29 | 0.02 | 0.00 | 0.03 | 0 | 0.3 |
| A27-2 | WS6 | 0 | 7.91 | 143.1 | 0.389 | | 8.6 | 3.3 | 0.38 | 0.20 | 0.01 | 0.05 | 0.01 | 1.06 |
| A27-2 | WS7 | 0 | 8.35 | 118.6 | 0.24 | | 6.9 | 1.5 | 0.36 | 0.08 | 0.01 | 0.04 | 0.01 | 0.14 |
| A27-2 | GRAB | | 8.52 | 135.1 | 0.35 | | 7.8 | 2.7 | 0.28 | 0.40 | 0.01 | 0.12 | 0.01 | 0.18 |
| A34-1 | WS4 | 0 | 7.02 | 17.86 | 0.12 | | 1.9 | 0.5 | 0.49 | 0.31 | 0.02 | 0.04 | 0.09 | 0.37 |
| A34-1 | WS5 | 0 | 5.61 | 22.5 | 0.017 | | 1.5 | 0.9 | 0.2 | 0.15 | 0.04 | 0.03 | 0.03 | 0.16 |
| A34-1 | WS5 | 3 | 6.01 | 20.8 | 0.021 | | 1.2 | 0.8 | 0.4 | 0.23 | 0.00 | 0.13 | 0.03 | 0.54 |
| A34-1 | WS7 | 0 | 6.91 | 34.3 | 0.023 | | 2.3 | 1.8 | 0.27 | 0.51 | 0.01 | 0.06 | 0 | 0.07 |
| A34-1 | GRAB | | 6.93 | 31.4 | 0.19 | | 2.1 | 2.4 | 0.32 | 0.04 | 0.01 | 0.05 | 0 | 0.06 |
| A34-1 | WS8 | 0 | 6.91 | 36.3 | 0.559 | | 1.8 | 1.9 | 0.35 | 0.16 | 0.00 | 0.05 | 0 | 0.47 |
| A34-1 | WS9 | 0 | 6.95 | 25.6 | 0.37 | | 2 | 1 | 0.34 | 0.22 | 0.01 | 0.05 | 0.02 | 0.25 |
| A34-1 | WS10 | 0 | 6.51 | 21.5 | 0.12 | | 1.3 | 0.8 | 0.5 | 0.22 | 0.21 | 0.04 | 1.85 | 1.89 |
| A34-1 | SD1 | | 8 | 82.7 | 0.58 | | 10.5 | 0.8 | 0.35 | 0.73 | 0.01 | 0.59 | 0.03 | 0.62 |
| A34-2 | WS6 | 0 | 8.31 | 106.2 | 0.028 | | 7.4 | 2.1 | 0.17 | 0.15 | 0.01 | 0.01 | 0.03 | 2.93 |
| A34-2 | SPRING | | 7.78 | 196.1 | 0.037 | | 11.4 | 4.2 | 0.41 | 0.24 | 0.02 | 0.28 | 0.02 | 0.38 |
| CR7-5C | SD4 | | 6.75 | 6.17 | 0.031 | | 1.1 | 0.4 | 0.17 | 0.37 | 0.09 | 0.36 | 0.04 | 0.32 |
| CR7-6 | WS2 | 0 | 5.64 | 4.22 | 0.47 | | 0.8 | 0.2 | 0.04 | 0.34 | 0.01 | 0.07 | 0.01 | 0.41 |
| CR7-6 | WS5 | 0 | 6.43 | 17.19 | 1.14 | | 1.7 | 0.7 | 0.35 | 0.43 | 0.08 | 0.32 | 0.02 | 0.43 |

Appendix 20: April Sampling Trip 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N(mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A17-1 | SD1 | | 6.88 | 51.6 | 0.01 | | 4.6 | 1.4 | 1.05 | 0.17 | 0.11 | 0.01 | 1.42 | 1.49 |
| A17-1 | SD5 | | 6.89 | 46.8 | 0.06 | | 4.7 | 0.8 | 2 | 0.12 | 0.12 | 0.05 | 0.18 | 0.85 |
| A17-2 | SD1 | | 6.86 | 11.07 | 0.5 | | 9.9 | 1.1 | 1.81 | 1.03 | 0.82 | 1.23 | 0.06 | 1.33 |
| A17-2 | WS1 | 0 | 7.46 | 61.5 | 0.04 | | 2.9 | 1.2 | 1.93 | 0.26 | 0.01 | 0.08 | 0 | 0.14 |
| A25-3 | GRAB | | 7.55 | 223 | 0.02 | | 5.7 | 15.2 | 0.38 | 0.05 | 0.00 | 0 | 0 | 3.26 |
| A25-3 | WS3 | 0 | 9.21 | 214 | 0.4 | | 5.3 | 12.8 | 0.28 | 1.99 | 0.05 | 0.04 | 0 | 0.37 |
| A27-1 | SD3 | | 6.89 | 37.3 | 0.06 | | 3.6 | 0.7 | 0.75 | 1.17 | 0.08 | 0 | 0 | 0.14 |
| A27-1 | SD5 | | 6.89 | 18 | 0.012 | | 5.5 | 1 | 0.38 | 0.12 | 0.04 | 0.39 | 0.02 | 0.81 |
| A34-1 | SD5 | | 6.33 | 47 | 0.025 | | 4.7 | 1.1 | 1.39 | 0.10 | 0.09 | 0.23 | 0.03 | 1.52 |
| A34-2 | SD5 | | 6.85 | 83.6 | 0.065 | | 8.6 | 1.3 | 1.55 | 2.22 | 0.02 | 0.06 | 0.17 | 0.81 |
| CR7-2 | WS1 | 0 | 7.65 | 91.8 | 0 | | 3.7 | 5.2 | 0.65 | 1.30 | 0.03 | 0.04 | 0 | 0.78 |
| CR7-5C | SD2 | | 7.31 | 63.5 | 0.549 | | 6.3 | 0.5 | 0.33 | 0.43 | 0.33 | 0 | 0.26 | 0.33 |
| CR7-5C | SD3 | | 6.66 | 39.6 | 0.089 | | 3.4 | 1.3 | 0.95 | 0.48 | 0.37 | 0 | 0.12 | 3.35 |
| CR7-5C | SD4 | | 5.76 | 34.1 | 0.04 | | 3.6 | 1.6 | 1.6 | 0.23 | 0.23 | 0 | 0.03 | 0.31 |
| CR7-5C | SD5 | | 6.47 | 51.9 | 0.06 | | 5.1 | 0.9 | 1.92 | 0.20 | 0.16 | 0 | 0.25 | 0.37 |
| CR7-6 | SD3 | | 6.78 | 52.5 | 0.1 | | 5.4 | 1.8 | 1.04 | 0.37 | 0.37 | 0.07 | 0.01 | 0.24 |

Appendix 21: May Sampling Trip 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N (mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A17-1 | SD1 | | 6.26 | 85.7 | 0.027 | | 5.6 | 1 | 11.95 | 1.00 | 1.00 | 0.14 | 0.02 | 4.54 |
| A17-2 | WS1 | 0 | 6.66 | 51.6 | 0.038 | | 2.7 | 1.1 | 1.87 | 0.15 | 0.09 | 0.22 | 0.08 | 2 |
| A17-2 | SD2 | | 6.22 | 66.2 | 0.012 | | 8.3 | 1 | 6.05 | 0.29 | 0.04 | 0 | 0.09 | 1.15 |
| A17-2 | SD5 | | 6.75 | 432 | 0.015 | | 4.7 | 1 | 12.78 | 0.33 | 0.08 | 1.6 | 0.11 | 1.82 |
| A17-2 | SD1 | | 6.41 | 66.5 | 0.031 | | 4 | 0.8 | 13.01 | 0.26 | 0.24 | 3.59 | 0 | 4.26 |
| A17-2 | SD3 | | 6.49 | 114.9 | 0.011 | | 5.8 | 4.8 | 4.2 | 1.61 | 1.21 | 1.28 | 0.12 | 4.43 |
| A25-2 | SD1 | | 6.07 | 113 | 0.037 | | 7.7 | 1.8 | 13.94 | 0.28 | 0.20 | 2.2 | 0.17 | 3.04 |
| A27-1 | WS3 | 0 | 8.23 | 382 | 0.316 | | 6 | 1 | 5.32 | 0.10 | 0.06 | 0.23 | 0.07 | 1.19 |
| A27-1 | WS4 | 0 | 7.92 | 241 | 0.087 | | 13.5 | 25 | 1.02 | 0.66 | 0.26 | 0.11 | 0.18 | 0.61 |
| A27-1 | WS7 | 0 | 7.82 | 186.2 | 0.013 | | 9.9 | 16 | 1.07 | 0.28 | 0.12 | 0.11 | 0 | 1.21 |
| A27-1 | SD1 | | 6.26 | 49.2 | 0.058 | | 11.5 | 2 | 0.47 | 0.28 | 0.17 | 0.78 | 0.08 | 10.04 |
| A27-2 | SD3 | | 6.82 | 133.2 | 0.014 | | 6.2 | 1.2 | 8.2 | 0.03 | 0.01 | 0.28 | 0.08 | 3.75 |
| A27-2 | SD1 | | 6.46 | 90.9 | 0.025 | | 5.8 | 0.8 | 6.8 | 1.16 | 0.58 | 0.14 | 0.31 | 1.16 |
| A27-2 | SD2 | | 6.47 | 80.9 | 0.019 | | 4.7 | 2.5 | 7.2 | 0.33 | 0.23 | 0.28 | 0.01 | 1.79 |
| A27-2 | WS6 | 0 | 7.42 | 263 | 0.02 | | 6.2 | 1.8 | 4.9 | 0.24 | 0.03 | 0.09 | 0 | 0.24 |
| A34-1 | WS3 | 0 | 6.82 | 87.9 | 0.006 | | 12.2 | 1.5 | 5.8 | 0.91 | 0.82 | 0.57 | 0 | 0.7 |
| A34-1 | SD3 | | 6.45 | 186.2 | 0.046 | | 4.8 | 2.2 | 4.5 | 0.79 | 0.60 | 3.57 | 0.02 | 4.79 |
| A34-2 | WS4 | 0 | 7.32 | 25.2 | 0.133 | | 6.2 | 4.8 | 5.8 | 0.75 | 0.68 | 0.56 | 0.07 | 1.08 |
| CR11-1 | SD5 | | 6.08 | 41.1 | 0.019 | | 3.1 | 0.8 | 6.12 | 0.36 | 0.13 | 0.03 | 0.06 | 1.05 |
| CR11-1 | SD1 | | 6.45 | 57.9 | 0.028 | | 5.3 | 1.1 | 5.93 | 0.50 | 0.43 | 0.25 | 0.08 | 1.66 |
| CR11-1 | SD3 | | 6.43 | 33.6 | 0.056 | | 3.2 | 0.7 | 3.58 | 0.51 | 0.30 | 0 | 0.11 | 5.57 |
| CR11-9 | WS1 | 0 | 8.31 | 149.1 | 0.094 | | 14 | 28 | 3.88 | 0.29 | 0.22 | 0.66 | 0.02 | 1.21 |
| CR7-2 | SD4 | | 6.92 | 53.9 | 0.033 | | 5 | 1 | 3.92 | 0.35 | 0.32 | 0.52 | 0.97 | 3.05 |
| CR7-2 | SD3 | | 6.82 | 98 | 0.044 | | 5.2 | 1.9 | 15.98 | 1.08 | 0.52 | 1.63 | 0.16 | 2.14 |
| CR7-5B | SD3 | | 6.35 | 23 | 0.022 | | 2.9 | 0.9 | 2.76 | 0.85 | 0.25 | 0.12 | 0.06 | 1.89 |
| CR7-5C | SD2 | | 6.12 | 51.8 | 0 | | 3.2 | 1.4 | 7.51 | 0.32 | 0.30 | 0.05 | 0.02 | 0.12 |
| CR7-5C | SD3 | | 6.61 | 34.2 | 0.039 | | 2.3 | 0.72 | 8.95 | 1.07 | 0.83 | 2 | 0.01 | 2.41 |
| CR7-5C | SD5 | | 6.19 | 46.6 | 0.009 | | 1.3 | 0.7 | 8.4 | 0.83 | 0.80 | 2.71 | 0.06 | 3.38 |
| CR7-6 | SD4 | | 6.17 | 46.9 | 0.025 | | 3.5 | 1.2 | 7.96 | 0.62 | 0.46 | 0.04 | 0.03 | 1.08 |

Appendix 22: June Sampling Trip 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N(mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A17-1 | SD5 | | | | 0.932 | 0.361 | | | | | | | | |
| A17-2 | SD1 | | | | 0.336 | 0.236 | | | | | | | | |
| A17-2 | SD2 | | | | 0.162 | 0.104 | | | | | | | | |
| A17-2 | SD3 | | | | 0.354 | 0.271 | | | | | | | | |
| A17-2 | SD5 | | | | 0.336 | 0.08 | | | | | | | | |
| A25-2 | SD5 | | | | 0.036 | 0.023 | | No Data due to Improper Data Collection and Preservation | | | | | | |
| A25-2 | SD4 | | | | 0.126 | 0.01 | | | | | | | | |
| A25-2 | SD1 | | | | 0.064 | 0.06 | | | | | | | | |
| A25-2 | SD4 | | | | 0.02 | 0.022 | | | | | | | | |
| A27-1 | SD5 | | | | 0.017 | 0.008 | | | | | | | | |
| A27-2 | SD2 | | | | 0.097 | 0.072 | | | | | | | | |
| A27-2 | SD1 | | | | 0.053 | 0.043 | | | | | | | | |
| A27-2 | WS6 | 0 | | | 0.014 | 0.003 | | | | | | | | |
| A34-1 | SD3 | | | | 0.014 | 0.007 | | | | | | | | |
| A34-1 | SD5 | | | | 0.161 | 0.023 | | | | | | | | |
| A34-2 | SD2 | | | | 0.07 | 0.056 | | | | | | | | |
| A34-2 | SD5 | | | | 0.368 | 0.025 | | | | | | | | |
| A34-2 | SD1 | | | | 0.07 | 0.006 | | | | | | | | |
| CR11-1 | SD2 | | | | 0.117 | 0.075 | | | | | | | | |
| CR7-2 | SD4 | | | | 0.174 | 0.015 | | | | | | | | |
| CR7-2 | SD4 | | | | 0.012 | 0.08 | | | | | | | | |
| CR7-5C | SD3 | | | | 0.039 | 0.027 | | | | | | | | |
| CR7-5C | SD5 | | | | 0.031 | 0.001 | | | | | | | | |
| CR7-6 | SD3 | | | | 0.218 | 0.033 | | | | | | | | |
| CR7-6 | SD2 | | | | 0.012 | 0.009 | | | | | | | | |
| CR7-6 | SD4 | | | | 0.07 | 0 | | | | | | | | |

Appendix 23: July Sampling Trip 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N(mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A25-2 | SD1 | | | | 0.004 | 0.002 | | | | | | | | |
| A25-2 | SD4 | | | | 0.007 | 0.003 | | | | | | | | |
| A25-2 | SD5 | | | | 0.003 | 0 | | | | | | | | |
| A25-3 | SD1 | | | | 0.003 | 0 | | | | | | | | |
| A25-3 | SD4 | | | | 0.006 | 0 | | | | | | | | |
| A27-2 | SD1 | | | | 0 | 0 | | | No Data due to Improper Data Collection and Preservation | | | | | |
| A27-2 | SD2 | | | | 0.008 | 0.001 | | | | | | | | |
| A34-1 | SD1 | | | | 0.051 | 0.011 | | | | | | | | |
| A34-1 | SD3 | | | | 0.02 | 0.008 | | | | | | | | |
| A34-1 | CONTROL | | | | 0.003 | 0 | | | | | | | | |
| A34-2 | SD4 | | | | 0.001 | 0 | | | | | | | | |
| CR11-1 | SD2 | | | | 0.002 | 0 | | | | | | | | |
| CR11-1 | SD4 | | | | 0.022 | 0.009 | | | | | | | | |
| CR11-3 | SD4 | | | | 0.016 | 0.006 | | | | | | | | |
| CR11-9 | SD1 | | | | 0.025 | 0.015 | | | | | | | | |
| CR11-9 | SD4 | | | | 0.036 | 0.023 | | | | | | | | |
| CR7-3B | SD1 | | | | 0.004 | 0 | | | | | | | | |
| CR7-5B | SD5 | | | | 0.013 | 0.007 | | | | | | | | |
| CR7-5B | CONTROL | | | | 0.008 | 0.006 | | | | | | | | |
| CR7-5C | SD1 | | | | 0.019 | 0.01 | | | | | | | | |
| CR7-5C | SD3 | | | | 0.023 | 0.013 | | | | | | | | |
| CR7-5C | SD4 | | | | 0.001 | 0 | | | | | | | | |
| CR7-5C | SD5 | | | | 0.025 | 0.012 | | | | | | | | |
| CR7-6 | SD3 | | | | 0.034 | 0.008 | | | | | | | | |

Appendix 24: August Sampling Trip (1 of 2) 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N (mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A17-1 | WS2 | 0 | 6.41 | 27.5 | 0.088 | 0.003 | 1.36 | 0.39 | 0.85 | 0.32 | 0.31 | 0 | 0.1 | 1.71 |
| A17-1 | CONTROL | | 5.62 | 28.5 | 0.022 | 0.012 | 1.57 | 0.32 | 2.51 | 0.11 | 0.10 | 0.26 | 0.05 | 1.59 |
| A17-1 | SD1 | 0 | 5.39 | 20.2 | 0.018 | 0.003 | 2.2 | 0.27 | 1.06 | 0.28 | 0.27 | 0 | 0.47 | 1.57 |
| A17-1 | WS1 | | 6 | 18.42 | 0.077 | 0.006 | 3.8 | 1.79 | 2.1 | 1.63 | 0.17 | 1.7 | 0.06 | 3.75 |
| A17-1 | SD5 | | 5.59 | 29.2 | 0.032 | 0.015 | 3.01 | 0.66 | 0.66 | 0.79 | 0.68 | 0 | 0.39 | 0.91 |
| A17-1 | SD4 | | 6.08 | 16.9 | 0.016 | 0.004 | 1.26 | 0.29 | 2.61 | 0.90 | 0.70 | 0.06 | 0.16 | 0.88 |
| A17-2 | SD5 | | 6.12 | 18.22 | 0.068 | 0.014 | 4.18 | 0.68 | 1.18 | 0.16 | 0.10 | 0.43 | 0.05 | 1.01 |
| A17-2 | SD1 | | 6.22 | 23.7 | 0.018 | 0.01 | 1.26 | 0.32 | 2.75 | 0.12 | 0.03 | 0 | 0.05 | 0.75 |
| A17-2 | WS7 | 0 | 6.21 | 23 | 0.259 | 0.204 | 9.64 | 4.41 | 4.58 | 0.93 | 0.21 | 0.24 | 0.07 | 2.91 |
| A17-2 | SD2 | | 6.33 | 103.5 | 0.095 | 0.034 | 3.75 | 0.68 | 2.21 | 0.13 | 0.09 | 0.23 | 0.02 | 4.5 |
| A17-2 | SD3 | | 5.67 | 34.6 | 0.018 | 0.01 | 2.75 | 0.44 | 1.86 | 0.88 | 0.05 | 0.29 | 0.13 | 1.25 |
| A25-2 | WS1 | 0 | 6.12 | 20.7 | 0.138 | 0.023 | 10.23 | 1.35 | 1.37 | 0.16 | 0.03 | 0 | 0.02 | 1.37 |
| A25-2 | SD1 | | 6.14 | 69.1 | 0.034 | 0.028 | 3.84 | 0.97 | 4.99 | 0.16 | 0.11 | 1.27 | 0.12 | 2.17 |
| A25-2 | SD4 | | 6.18 | 23.9 | 0.011 | 0.006 | 2.19 | 0.42 | 3.35 | 0.15 | 0.05 | 0.02 | 0.02 | 0.81 |
| A25-2 | WS2 | 3 | 5.78 | 19.6 | 0.021 | 0.002 | 2.46 | 0.73 | 1.43 | 0.11 | 0.08 | 0.12 | 0.01 | 0.29 |
| A25-2 | SD2 | | 5.58 | 22.1 | 0.039 | 0.02 | 4.37 | 0.74 | 3.39 | 0.16 | 0.14 | 0.23 | 0.08 | 2.1 |
| A25-2 | SD5 | | 5.98 | 28.2 | 0.026 | 0.01 | 2.17 | 0.45 | 5.71 | 0.14 | 0.12 | 0 | 0.13 | 1.63 |
| A25-3 | WS1 | 0 | 6.16 | 30.4 | 0.014 | 0.003 | 3.12 | 0.89 | 2.06 | 0.48 | 0.11 | 0.35 | 0.08 | 3.59 |
| A25-3 | SD1 | | 5.76 | 44.6 | 0.018 | 0.01 | 3.32 | 0.69 | 4.69 | 0.26 | 0.26 | 0.54 | 0.06 | 5.38 |
| A27-1 | SD1 | | 5.89 | 33.2 | 0.248 | 0.06 | 5.58 | 0.95 | 2.74 | 0.09 | 0.07 | 0.01 | 0.2 | 4 |
| A27-2 | SD1 | | 6.02 | 36.3 | 0.012 | 0.003 | 4.45 | 0.8 | 5.94 | 0.13 | 0.37 | 0.06 | 0.58 | 7.71 |
| A27-2 | SD4 | | 6.07 | 42.2 | 0.094 | 0.018 | 8.75 | 1.47 | 11.39 | 0.21 | 0.11 | 0.71 | 3.7 | 4.23 |
| A27-2 | SD2 | | 6.32 | 98.8 | 0.018 | 0.009 | 4.08 | 0.9 | 4.22 | 1.11 | 0.97 | 0.23 | 0.33 | 0.95 |
| A34-1 | CONTROL | | 6.13 | 38.9 | 0.015 | 0.004 | 1.38 | 0.3 | 1.23 | 0.10 | 0.02 | 0.2 | 0.04 | 1.09 |
| A34-1 | SD3 | | 5.62 | 14.56 | 0.018 | 0.01 | 1.67 | 0.54 | 2.6 | 0.83 | 0.02 | 0 | 0.06 | 2.99 |
| A34-1 | SD5 | | 5.95 | 19.78 | 0.134 | 0.108 | 1.76 | 0.51 | 3.05 | 0.27 | 0.16 | 0.69 | 0.06 | 1.2 |
| A34-2 | SD4 | | 5.42 | 20.3 | 0.065 | 0.018 | 2.29 | 0.58 | 2.18 | 0.06 | 0.09 | 0.15 | 0.04 | 0.99 |

Appendix 24 (continued): August Sampling Trip (2 of 2) 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N (mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CR11-1 | SD2 | | 6.33 | 17.33 | 0.019 | 0.007 | 3.47 | 0.44 | 1.38 | 0.13 | 0.10 | 0.04 | 0.26 | 1.03 |
| CR11-1 | SD1 | | 6.12 | 20.1 | 0.017 | 0.009 | 2.54 | 0.54 | 2.54 | 0.12 | 0.06 | 0.19 | 0.06 | 2.05 |
| CR11-1 | SD4 | | 5.86 | 19.89 | 0.005 | 0.001 | 1.35 | 0.36 | 1.68 | 0.13 | 0.06 | 0.06 | 0.02 | 1.14 |
| CR11-1 | SD5 | | 5.65 | 14.3 | 0.024 | 0.015 | 1.93 | 0.48 | 1.77 | 0.41 | 0.08 | 0.08 | 0.3 | 2.77 |
| CR11-3 | SD1 | | 6.18 | 19.9 | 0.015 | 0.01 | 4.54 | 0.87 | 4.98 | 0.09 | 0.05 | 0.09 | 0.17 | 3.49 |
| CR11-3 | SD5 | | 6.15 | 36.5 | 0.023 | 0.005 | 1.29 | 0.34 | 1.34 | 0.62 | 0.02 | 0.01 | 0.17 | 2.29 |
| CR11-3 | SD4 | | 6.16 | 19.7 | 0.089 | 0.056 | 8.22 | 1.03 | 4.49 | 0.06 | 0.06 | 0.33 | 2.45 | 6.21 |
| CR11-3 | WS1 | 0 | 5.55 | 69.5 | 0.037 | 0.009 | 5.2 | 1.99 | 2.41 | 3.35 | 1.76 | 0.05 | 0.06 | 1.18 |
| CR11-9 | SD1 | | 6.23 | 36.5 | 0.018 | 0.008 | 4.81 | 1.77 | 6.57 | 0.61 | 0.45 | 0 | 1.54 | 3.44 |
| CR11-9 | SD4 | | 6.29 | 53 | 0.015 | 0.007 | 4.07 | 0.73 | 0.85 | 0.19 | 0.15 | 2.17 | 1.26 | 1.78 |
| CR7-2 | SD3 | | 6.55 | 27.9 | 0.012 | 0.006 | 4.62 | 1.22 | 2.91 | 1.16 | 1.04 | 0 | 0.01 | 1.29 |
| CR7-5B | SD5 | | 6.39 | 10.42 | 0.007 | 0.007 | 1.62 | 0.39 | 0.59 | 0.18 | 0.14 | 0.06 | 0.03 | 0.13 |
| CR7-5B | SD1 | | 5.81 | 18.86 | 0.005 | 0.001 | 2.96 | 0.44 | 1.38 | 0.08 | 0.06 | 1.73 | 0.23 | 2.66 |
| CR7-5B | WS7 | 0 | 6.48 | 52.88 | 0.025 | 0.013 | 9.04 | 1.14 | 3.21 | 0.05 | 0.01 | 0.2 | 0.05 | 3.46 |
| CR7-5B | CONTROL | | 6.19 | 25.5 | 0.035 | 0.023 | 0.71 | 0.18 | 0.42 | 0.19 | 0.18 | 0.24 | 0.02 | 1.49 |
| CR7-5C | WS3 | 0 | 6.11 | 33.3 | 0.017 | 0.02 | 3.56 | 1.13 | 2.62 | 0.38 | 0.02 | 0.31 | 0.01 | 4.62 |
| CR7-5C | SD1 | | 6.69 | 10.92 | 0.014 | 0.006 | 1.61 | 0.44 | 2.12 | 0.57 | 0.48 | 0 | 0.53 | 1.03 |
| CR7-5C | SD3 | | 6.06 | 11.15 | 0.024 | 0.009 | 1.44 | 0.44 | 2.16 | 0.36 | 0.19 | 0.15 | 0.01 | 0.67 |
| CR7-5C | WS2 | 0 | 6.38 | 19.45 | 0.151 | 0.013 | 2.04 | 0.67 | 0.87 | 0.72 | 0.39 | 0.06 | 0 | 1.69 |
| CR7-5C | SD4 | | 6.2 | 20 | 0.002 | 0.001 | 3.52 | 0.56 | 1.8 | 0.13 | 0.06 | 0.04 | 0.14 | 0.99 |
| CR7-6 | WS5 | 0 | 6.14 | 23.7 | 0.046 | 0.012 | 2.21 | 0.9 | 1.09 | 0.56 | 0.37 | 0.13 | 0.02 | 1.19 |
| CR7-6 | WS4 | 0 | 5.78 | 18.5 | 0.027 | 0.014 | 2.01 | 0.85 | 1.6 | 0.12 | 0.08 | 0.61 | 0.04 | 1.51 |
| CR7-6 | SD2 | | 5.39 | 19.8 | 0.074 | 0.045 | 7.85 | 1.52 | 2.78 | 0.15 | 0.03 | 0.2 | 0.47 | 2.52 |
| CR7-6 | WS2 | 0 | 6.7 | 46.4 | 0.04 | 0.028 | 1.22 | 0.66 | 1.93 | 0.24 | 0.14 | 0.05 | 0.03 | 0.93 |
| CR7-6 | SD3 | | 5.33 | 12.3 | 0.037 | 0.009 | 2.34 | 0.61 | 1.65 | 0.34 | 0.28 | 0.37 | 0.3 | 1.03 |
| CR7-6 | SD4 | | 6.26 | 19.45 | 0.052 | 0.014 | 2.79 | 0.68 | 0.78 | 0.26 | 0.14 | 0 | 0.24 | 1.77 |

Appendix 25: September Sampling Event (1 of 2) 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N (mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A17-1 | WS3 | 0 | 6.62 | 25.1 | 0.062 | 0.012 | 1.98 | 0.88 | 1.39 | 0.84 | 1.49 | 0.7 | 0.39 | 3.74 |
| A17-1 | SD5 | | 6.18 | 24.7 | 0.231 | 0.021 | 4.2 | 1.01 | 2.18 | 0.37 | 0.30 | 0.01 | 1.23 | 3.74 |
| A17-1 | SD1 | | 5.85 | 11.91 | 0.04 | 0.019 | 2.99 | 0.33 | 0.93 | 0.08 | 0.03 | 0.33 | 0.09 | 0.78 |
| A17-1 | CONTROL | | 6.23 | 15.28 | 0.031 | 0.019 | 3.11 | 0.6 | 4.67 | 0.13 | 0.19 | 0.48 | 0.03 | 1.81 |
| A17-1 | SD4 | | 6.63 | 19.33 | 0.026 | 0.013 | 2.75 | 0.47 | 1.79 | 0.15 | 0.11 | 0.03 | 0.56 | 1.57 |
| A17-1 | SD1 | | 6.52 | 28.5 | 0.287 | 0.165 | 3.41 | 0.56 | 2.13 | 0.09 | 0.07 | 0.56 | 1.12 | 2.2 |
| A17-2 | SD3 | | 6.61 | 57.6 | 0.019 | 0.013 | 1.49 | 0.4 | 4.08 | 0.39 | 0.15 | 0.4 | 0.25 | 1.41 |
| A17-2 | SD5 | | 6.62 | 23.4 | 0.122 | 0.116 | 1.27 | 0.35 | 1.5 | 0.15 | 0.14 | 0.12 | 0.89 | 2.27 |
| A25-2 | SD1 | | 6.29 | 38.5 | 0.012 | 0.003 | 3.41 | 0.61 | 2.39 | 0.18 | 0.22 | 0 | 0.86 | 3.65 |
| A25-2 | SD2 | | 6.32 | 28.5 | 0.007 | 0.003 | 2.09 | 0.4 | 2.54 | 0.15 | 0.05 | 0.04 | 0.12 | 0.97 |
| A25-2 | SD5 | | 6.26 | 18.61 | 0.003 | 0.003 | 8.13 | 0.97 | 12.83 | 0.63 | 0.15 | 1.2 | 0.52 | 0.8 |
| A25-3 | SD3 | | 6.09 | 21.5 | 0.051 | 0.015 | 4.92 | 0.97 | 3.41 | 0.43 | 0.41 | 0.61 | 0.62 | 1.57 |
| A25-3 | SD1 | | 6.44 | 27.5 | 0.033 | 0.019 | 10.68 | 1.58 | 14.74 | 0.60 | 0.47 | 0 | 0.09 | 0.73 |
| A27-1 | SD1 | | 6.39 | 26 | 0.033 | 0.014 | 2.62 | 0.57 | 1.86 | 0.06 | 0.02 | 0.04 | 0.16 | 1.61 |
| A27-1 | SD3 | | 6.16 | 12.67 | 0.041 | 0.011 | 3.26 | 0.64 | 2.66 | 0.19 | 0.14 | 0.05 | 0.09 | 0.99 |
| A27-2 | SD2 | | 6.32 | 23.4 | 0.048 | 0.011 | 8.64 | 1.08 | 8.1 | 0.16 | 0.10 | 0.73 | 0.24 | 1.69 |
| A27-2 | SD4 | | 6.33 | 25.73 | 0.101 | 0.057 | 11.61 | 2.77 | 5.84 | 0.05 | 0.03 | 2.07 | 1.38 | 2.58 |
| A27-2 | SD1 | | 6.6 | 19.18 | 0.287 | 0.025 | 4.24 | 1.48 | 10.19 | 0.20 | 0.15 | 0.3 | 0.08 | 0.45 |
| A34-1 | CONTROL | | 6.78 | 32.5 | 0.027 | 0.016 | 1.01 | 0.28 | 1.73 | 0.08 | 0.06 | 0.05 | 0.04 | 1.48 |
| A34-1 | SD1 | | 6.32 | 37.6 | 0.039 | 0.023 | 4.68 | 0.9 | 2.84 | 0.12 | 0.08 | 0.14 | 0.35 | 1.12 |
| A34-1 | SD5 | | 6.07 | 16.76 | 0.064 | 0.023 | 1.76 | 0.47 | 2.52 | 0.31 | 0.29 | 0.14 | 0.13 | 2.14 |
| A34-1 | SD3 | | 6.79 | 18.96 | 0.031 | 0.02 | 8.54 | 1.08 | 6.98 | 0.10 | 0.06 | 0.22 | 0.69 | 1.26 |

Appendix 25 (continued): September Sampling Event (2 of 2) 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH4-N (mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CR11-1 | SD4 | | 6.52 | 9.71 | 0.014 | 0.008 | 2.19 | 1.08 | 1.47 | 0.71 | 0.61 | 0.17 | 0.08 | 0.63 |
| CR11-1 | SD2 | | 6.88 | 17.63 | 0.014 | 0.003 | 3 | 1.44 | 1.38 | 0.34 | 0.05 | 0.27 | 0.12 | 2.58 |
| CR11-3 | WS1 | 0 | 6.48 | 16.17 | 0.064 | 0.022 | 5.2 | 1.99 | 2.41 | 0.16 | 0.11 | 0.12 | 0.02 | 0.8 |
| CR11-3 | SD5 | | 6.32 | 27.3 | 0.036 | 0.022 | 12.62 | 6.32 | 2.47 | 0.18 | 0.16 | 0.26 | 0.15 | 0.62 |
| CR11-3 | SD1 | | 6.18 | 21.6 | 0.047 | 0.023 | 1.47 | 0.32 | 2.82 | 0.48 | 0.21 | 0.26 | 0.39 | 1.3 |
| CR11-9 | SD2 | | 6.18 | 37 | 0.04 | 0.002 | 5.48 | 0.68 | 2.59 | 0.07 | 0.02 | 0.6 | 0.82 | 1.21 |
| CR11-9 | SD4 | | 6.53 | 18.57 | 0.022 | 0.012 | 1.97 | 0.48 | 1.84 | 0.84 | 1.49 | 0.38 | 0.3 | 0.62 |
| CR11-9 | SD1 | | 6.45 | 19.6 | 0.048 | 0.031 | 3.47 | 1.31 | 4.26 | 0.26 | 0.12 | 1.12 | 1.23 | 3.43 |
| CR7-2 | SD3 | | 6.74 | 18.522 | 0.218 | 0.057 | 7.54 | 2.11 | 18.1 | 0.12 | 0.06 | 2.07 | 0.05 | 2.58 |
| CR7-5B | CONTROL | | 6.61 | 8.48 | 0.025 | 0.007 | 3.37 | 1.09 | 2.12 | 0.07 | 0.07 | 0.03 | 0.08 | 0.82 |
| CR7-5C | SD4 | | 6.6 | 18.69 | 0.007 | 0.006 | 1.12 | 0.52 | 3.38 | 0.30 | 0.24 | 0.04 | 0.49 | 1.94 |
| CR7-5C | SD3 | | 5.92 | 16.15 | 0.012 | 0.006 | 4.34 | 0.94 | 3.42 | 0.90 | 0.88 | 0.05 | 1.38 | 2.55 |
| CR7-5C | SD5 | | 6.21 | 21.6 | 0.008 | 0.003 | 1.6 | 0.41 | 3.98 | 0.52 | 0.50 | 0.05 | 0.82 | 1.99 |
| CR7-6 | SD3 | | 6.62 | 19.62 | 0.181 | 0.062 | 5.02 | 0.76 | 1.54 | 0.30 | 0.25 | 0.07 | 0.83 | 0.91 |
| CR7-6 | SD4 | | 6.31 | 38.1 | 0.091 | 0.033 | 3.83 | 0.94 | 1.74 | 0.24 | 0.22 | 0.11 | 0.56 | 2.24 |
| CR7-6 | SD2 | | 6.73 | 11.6 | 0.114 | 0.041 | 1.11 | 0.22 | 2.14 | 0.47 | 0.15 | 0.06 | 0.53 | 1.4 |

Appendix 26: November Sampling Event (1 of 5) 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N(mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A17-1 | WS4 | 6 | 5.46 | 18.44 | 0.118 | 0.114 | 1.61 | 0.63 | 1.73 | 0.73 | 0.03 | 0.00 | 0.00 | 2.30 |
| A17-1 | WS4 | 3 | 5.59 | 19.33 | 0.025 | 0.025 | 1.80 | 0.65 | 1.63 | 0.06 | 0.02 | 0.00 | 0.05 | 1.04 |
| A17-1 | WS3 | 0 | 5.51 | 18.01 | 0.058 | 0.021 | 1.28 | 0.65 | 0.96 | 0.12 | 0.03 | 0.15 | 0.02 | 0.18 |
| A17-1 | Control | | 5.89 | 19.76 | 0.003 | 0.015 | 0.05 | 0.02 | 0.03 | 0.28 | 0.26 | 0.16 | 0.02 | 1.48 |
| A17-1 | SD3 | | 6.06 | 17.32 | 0.035 | 0.023 | 1.66 | 0.86 | 1.74 | 0.09 | 0.07 | 0.14 | 0.04 | 0.29 |
| A17-1 | WS3 | 6 | 6.15 | 24.50 | 0.135 | 0.026 | 1.33 | 0.33 | 4.24 | 1.04 | 0.19 | 0.02 | 0.06 | 1.65 |
| A17-1 | WS4 | 0 | 6.67 | 33.40 | 0 | 0 | 1.28 | 0.65 | 0.96 | 0.36 | 0.34 | 0.00 | 0.04 | 1.58 |
| A17-2 | WS1 | 0 | 6.03 | 21.50 | 0.028 | 0.026 | 1.55 | 0.31 | 2.61 | 0.22 | 0.19 | 0.16 | 0.01 | 1.92 |
| A17-2 | WS7 | 0 | 6.82 | 95.40 | 0.274 | 0.256 | 2.68 | 0.91 | 1.71 | 0.63 | 0.35 | 0.88 | 0.01 | 2.75 |
| A17-2 | WS7 | 3 | 7.31 | 79.80 | 0.019 | 0.017 | 5.74 | 0.78 | 2.01 | 0.25 | 0.06 | 0.01 | 0.02 | 0.31 |
| A17-1 | WS3 | 3 | 5.47 | 18.62 | 0.018 | 0.019 | 1.54 | 0.58 | 1.29 | 0.08 | 0.02 | 0.04 | 0.00 | 2.91 |
| A17-1 | WS1 | 0 | 5.33 | 19.16 | 0.031 | 0.031 | 0.06 | 0.01 | 0.02 | 0.16 | 0.07 | 0.00 | 0.04 | 1.75 |
| A17-1 | SD1 | | 5.58 | 15.03 | 0.078 | 0.078 | 0.08 | 0.04 | 0.05 | 0.62 | 0.53 | 0.00 | 0.09 | 4.26 |
| A17-1 | WS1 | 3 | 5.79 | 19.32 | 0.023 | 0.029 | 0.06 | 0.01 | 0.02 | 0.06 | 0.04 | 0.00 | 0.00 | 1.42 |
| A25-2 | SD4 | | 6.4 | 20.3 | 0.001 | 0.015 | 0.04 | 0.01 | 0.03 | 0.02 | 0.01 | 0.00 | 0.00 | 2.64 |
| A25-2 | WS4 | 0 | 6.86 | 44.1 | 0.696 | 0.182 | 3.95 | 0.97 | 2.73 | 0.71 | 0.64 | 0.00 | 0.03 | 2.85 |
| A25-2 | WS1 | 3 | 7.06 | 27.7 | 0.028 | 0.023 | 2.58 | 0.90 | 2.51 | 0.08 | .08 | 0.01 | 0.04 | 0.65 |
| A25-3 | SD3 | 0 | 6.13 | 23 | 0.02 | 0.021 | 2.66 | 0.76 | 1.69 | 0.08 | 0.01 | 0.09 | 0.00 | 1.82 |
| A25-3 | WS5 | 0 | 6.52 | 44.5 | 0.087 | 0.097 | 1.32 | 0.47 | 1.84 | 1.04 | 0.56 | 0.88 | 0.01 | 4.48 |
| A25-3 | WS5 | 0 | 6.2 | 24.7 | 0.05 | 0.046 | 1.76 | 0.73 | 1.54 | 0.21 | 0.18 | 0.02 | 0.03 | 2.12 |
| A25-2 | WS1 | 6 | 6.46 | 38.70 | 0.077 | 0.034 | 3.79 | 1.17 | 2.74 | 0.13 | 0.06 | 0.05 | 0.20 | 1.65 |
| A25-2 | WS4 | 3 | 6.19 | 26.20 | 0.067 | 0.025 | 2.67 | 0.65 | 3.00 | 0.04 | 0.03 | 0.01 | 0.02 | 1.25 |
| A34-1 | WS4 | 0 | 6.32 | 24.7 | 0.016 | 0.013 | 2.30 | 0.76 | 1.32 | 0.03 | 0.02 | 0.04 | 0.03 | 0.48 |

Appendix 26 (continued): November Sampling Event (2 of 5) 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N (mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A34-1 | WS8 | 6 | 6.65 | 30.9 | 0.015 | 0.02 | 3.14 | 1.88 | 1.38 | 0.05 | 0.01 | 0.02 | 0.03 | 0.98 |
| A34-1 | WS1 | 3 | 6.36 | 20.3 | 0.018 | 0.018 | 2.09 | 0.70 | 0.76 | 0.12 | 0.12 | 0.76 | 0.15 | 1.41 |
| A34-1 | WS5 | 0 | 6.51 | 21.8 | 0.025 | 0.021 | 1.70 | 0.81 | 1.01 | 0.15 | 0.04 | 0.03 | 0.00 | 1.13 |
| A34-1 | SD3 | | 6.44 | 15.23 | 0.008 | 0.016 | 0.97 | 0.32 | 2.53 | 0.19 | 0.03 | 0.02 | 0.05 | 0.38 |
| A34-1 | WS5 | 3 | 5.93 | 21.9 | 0.052 | 0.035 | 1.71 | 0.67 | 1.26 | 0.16 | 0.00 | 0.02 | 0.03 | 0.49 |
| A34-1 | WS2 | 0 | 4.9 | 19.8 | 0.038 | 0.042 | 1.14 | 0.65 | 1.38 | 0.06 | 0.06 | 0.01 | 0.04 | 7.79 |
| A34-1 | WS9 | 0 | 5.98 | 21.7 | 0.03 | 0.021 | 1.63 | 0.82 | 0.94 | 0.11 | 0.10 | 0.00 | 0.00 | 0.62 |
| A34-1 | WS4 | 3 | 6.48 | 28.5 | 0 | 0.052 | 2.82 | 0.99 | 2.38 | 0.06 | 0.06 | 0.02 | 0.02 | 1.98 |
| A34-1 | CONTROL | | 5.83 | 18.35 | 0.021 | 0.031 | 0.88 | 0.34 | 4.04 | 0.04 | 0.04 | 0.01 | 0.07 | 4.23 |
| A34-2 | WS2 | 0 | 5.89 | 23.7 | 0.026 | 0.014 | 2.11 | 0.81 | 0.88 | 0.05 | 0.02 | 0.16 | 0.04 | 2.15 |
| A34-2 | WS6 | 0 | 6.18 | 26.4 | 0.016 | 0.02 | 1.95 | 0.86 | 0.92 | 0.06 | 0.01 | 0.02 | 0.00 | 0.28 |
| A34-2 | SD5 | | 5.71 | 16.89 | 0.026 | 0.021 | 0.80 | 0.22 | 2.94 | 0.06 | 0.03 | 0.02 | 0.04 | 0.81 |
| A34-2 | WS4 | 0 | 5.29 | 18.61 | 0.054 | 0.02 | 0.70 | 0.73 | 1.09 | 0.16 | 0.02 | 0.01 | 0.03 | 1.23 |
| A34-2 | WS3 | 0 | 6.48 | 68.30 | 0.051 | 0 | 7.72 | 4.49 | 0.58 | 0.03 | 0.03 | 0.08 | 0.01 | 0.27 |
| A34-2 | WS5 | 0 | 6.02 | 24 | 0.06 | 0.062 | 7.63 | 3.96 | 1.84 | 0.53 | 0.15 | 0.01 | 0.08 | 3.26 |
| A34-1 | WS10 | 0 | 6.6 | 45.70 | 0.043 | 0.037 | 0.06 | 0.01 | 0.09 | 0.17 | 0.17 | 0.00 | 0.00 | 1.51 |
| A34-1 | WS6 | 0 | 5.32 | 17.41 | 0.013 | 0.021 | 2.98 | 1.69 | 1.04 | 0.01 | 0.00 | 0.02 | 0.00 | 0.70 |
| A34-2 | WS7 | 0 | 7.88 | 72.80 | 0.035 | 0.024 | 1.40 | 0.68 | 0.86 | 0.14 | 0.01 | 0.01 | 0.04 | 0.61 |
| CR - 106 (2) | | | 8.27 | 169.9 | 0.035 | 0.023 | 7.72 | 4.49 | 0.58 | 0.03 | 0.03 | 0.03 | 0.05 | 3.91 |
| CR -106 | GRAB | | 9.08 | 135.10 | 0.101 | 0.026 | 10.66 | 9.83 | 1.42 | 0.05 | 0.03 | 0.06 | 0.03 | 3.47 |
| CR11- 3 | SD5 | | 5.81 | 42.2 | 0.020 | 0.025 | 3.74 | 0.84 | 6.08 | 0.20 | 0.14 | 0.89 | 0.18 | 3.54 |
| CR11- 3 | WS2 | 0 | 5.94 | 23.5 | 0.050 | 0.021 | 2.16 | 1.03 | 1.76 | 0.20 | 0.08 | 0.02 | 0.00 | 1.03 |
| CR11- 3 | GRAB | | 6.63 | 31 | 0.183 | 0.156 | 3.43 | 1.47 | 1.05 | 0.13 | 0.04 | 0.01 | 0.00 | 0.81 |
| CR11- 9 | SD4 | | 6.63 | 27.10 | 0.045 | 0.045 | 8.09 | 4.43 | 1.50 | 0.06 | 0.00 | 0.05 | 0.09 | 2.24 |
| CR11- 9 | WS1 | 0 | 7.45 | 114.8 | 0.045 | 0.040 | 13.34 | 5.13 | 2.63 | 0.28 | 0.25 | 0.02 | 0.03 | 0.82 |

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N (mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CR11-9 | WS2 | 0 | 6.29 | 24 | 0.074 | 0.073 | 1.56 | 0.39 | 2.33 | 0.14 | 0.01 | 0.02 | 0.01 | 5.36 |
| CR11-9 | SD1 | | 6.6 | 35.8 | 0.007 | 0.017 | 2.04 | 0.70 | 5.99 | 0.10 | 0.01 | 0.01 | 0.03 | 0.74 |
| CR11-9 | WS1 | 3 | 7.23 | 143.90 | 0.026 | 0.026 | 19.65 | 5.42 | 3.64 | 0.06 | 0.05 | 1.41 | 0.35 | 1.81 |
| CR11-9 | SD2 | | 6.22 | 17.28 | 0.009 | 0.018 | 1.56 | 0.39 | 2.33 | 0.48 | 0.29 | 0.02 | 0.03 | 0.37 |
| CR11-3 | SD1 | | 6.12 | 14.74 | 0.013 | 0.025 | 1.44 | 0.69 | 0.84 | 0.07 | 0.03 | 0.01 | 0.06 | 0.41 |
| CR11-3 | WS6 | 0 | 6.73 | 31.8 | 0.023 | 0.014 | 3.16 | 1.63 | 0.95 | 0.06 | 0.06 | 0.01 | 0.00 | 0.53 |
| CR11-3 | WS1 | 0 | 6.7 | 33.5 | 0.026 | 0.035 | 3.09 | 1.32 | 1.24 | 0.27 | 0.02 | 0.01 | 0.00 | 0.56 |
| CR7-2 | GRAB | | 9.17 | 93.6 | 0.027 | 0.014 | 5.61 | 6.42 | 0.78 | 0.04 | 0.01 | 0.04 | 0.00 | 2.69 |
| CR7-5B | SD1 | | 5.92 | 37.90 | 0.043 | 0.038 | 1.01 | 0.44 | 4.02 | 0.85 | 0.45 | 0.47 | 0.05 | 1.93 |
| CR7-5B | WS5 | 6 | 5.95 | 27.5 | 0.039 | 0.021 | 2.33 | 0.81 | 3.1 | 0.09 | 0.07 | 0.08 | 0.00 | 0.74 |
| CR7-2 | SD2 | | 8.77 | 46.20 | 0.076 | 0.076 | 6.28 | 0.75 | 3.72 | 0.17 | 0.07 | 0.06 | 0.01 | 0.71 |
| CR7-2 | WS6 | 3 | 6.77 | 40.00 | 0.030 | 0.019 | 3.99 | 1.80 | 1.60 | 0.05 | 0.05 | 0.01 | 0.00 | 0.78 |
| CR7-2 | WS4 | 3 | 6.22 | 31.2 | 0.006 | 0.013 | 3.17 | 1.3 | 2.87 | 0.08 | 0.05 | 0.37 | 0.03 | 0.51 |
| CR7-2 | WS2 | 0 | 6.5 | 113.8 | 0.112 | 0.099 | 2.01 | 0.66 | 1.19 | 1.42 | 0.19 | 0.03 | 0.11 | 1.30 |
| CR7-5B | WS5 | 3 | 6.11 | 27.8 | 0.048 | 0.023 | 3.99 | 0.87 | 2.96 | 0.25 | 0.24 | 0.03 | 0.04 | 1.69 |
| CR7-5B | WS3 | 0 | 5.87 | 22.7 | 0.979 | 0.07 | 2.08 | 0.7 | 1.42 | 0.05 | 0.04 | 0.11 | 0.03 | 2.97 |
| CR7-5B | WS1 | 0 | 6.53 | 30.7 | 0.011 | 0.019 | 7.59 | 3.15 | 1.1 | 0.14 | 0.11 | 0.03 | 0.68 | 1.55 |
| CR7-5C | WS5 | 6 | 6.48 | 21.40 | 0.664 | 0.158 | 0.99 | 0.31 | 4.08 | 0.14 | 0.04 | 0.30 | 0.03 | 1.02 |
| CR7-5C | WS4 | 0 | 6.01 | 17.81 | 0.117 | 0.078 | 1.45 | 0.62 | 1.08 | 0.21 | 0.07 | 0.63 | 0.03 | 0.67 |
| CR7-5C | WS5 | 3 | 6.29 | 20.5 | 0.025 | 0.021 | 1.68 | 0.61 | 1.55 | 0.06 | 0.01 | 0.09 | 0.00 | 1.49 |
| CR7-5C | SD4 | | 6.86 | 31.60 | 0.005 | 0.016 | 0.94 | 0.51 | 5.96 | 0.32 | 0.06 | 0.02 | 0.03 | 0.47 |
| CR7-5C | WS6 | 3 | 6.23 | 21.1 | 0.026 | 0.021 | 1.7 | 0.65 | 2.14 | 0.37 | 0.06 | 0.02 | 0.00 | 0.39 |
| CR7-5C | SD3 | | 6.28 | 23 | 0.002 | 0.014 | 1.47 | 0.52 | 5.16 | 0.49 | 0.04 | 0.01 | 0.05 | 0.58 |
| CR7-5C | SD5 | | 6.33 | 32.5 | 0.009 | 0.018 | 0.09 | 0.01 | 0.05 | 0.66 | 0.43 | 0.12 | 0.06 | 0.93 |
| CR7-5C | WS2 | 0 | 6.31 | 23 | 0.019 | 0.016 | 3.57 | 0.74 | 1.23 | 0.10 | 0.05 | 0.18 | 0.05 | 0.94 |

Appendix 26 (continued): November Sampling Event (4 of 5) 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH3-N(mg/L) | NO3 (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CR7-6 | WS2 | 0 | 5.5 | 17.44 | 0.020 | 0.024 | 1.08 | 0.53 | 1.26 | 0.03 | 0.02 | 0.04 | 0.02 | 0.23 |
| CR7-6 | WS5 | 0 | 6.11 | 18.29 | 0.116 | 0.012 | 1.25 | 0.64 | 0.54 | 0.10 | 0.03 | 0.08 | 0.02 | 0.30 |
| CR7-6 | WS3 | 0 | 6.73 | 25.3 | 0.742 | 0.167 | 2.42 | 0.71 | 1.72 | 0.12 | 0.06 | 0.15 | 0.00 | 1.39 |
| CR7-6 | SD4 | | 6.74 | 22.4 | 0.027 | 0.031 | 2.01 | 0.4 | 2.87 | 0.08 | 0.04 | 0.00 | 0.02 | 0.61 |
| CR7-6 | WS4 | 6 | 6.7 | 36.9 | 0.033 | 0.023 | 6.06 | 1.17 | 2.43 | 0.82 | 0.82 | 0.00 | 0.01 | 0.84 |
| CR7-2 | WS5 | 0 | 6.81 | 42.20 | 0.042 | 0.045 | 9.27 | 1.23 | 1.62 | 0.61 | 0.45 | 0.00 | 0.00 | 0.53 |
| CR7-2 | SD4 | | 6.55 | 19.90 | 0.016 | 0.016 | 3.49 | 0.66 | 0.93 | 0.40 | 0.03 | 0.01 | 0.04 | 2.05 |
| CR7-2 | WS4 | 0 | 6.96 | 59 | 0.121 | 0.064 | 9.27 | 1.23 | 1.62 | 1.21 | 1.19 | 0.32 | 0.04 | 1.55 |
| CR7-5B | WS6 | 3 | 6.8 | 32.90 | 0.092 | 0.041 | 4.61 | 0.79 | 1.91 | 0.47 | 0.45 | 0.02 | 0.00 | 0.18 |
| CR7-5B | WS6 | 6 | 6.26 | 18.28 | 0.078 | 0.07 | 3.89 | 0.43 | 1.23 | 0.03 | 0.02 | 0.00 | 0.02 | 0.86 |
| CR7-5B | CONTROL | | 5.92 | 33.90 | 0.022 | 0.028 | 0.75 | 0.29 | 3.99 | 0.36 | 0.19 | 0.18 | 0.02 | 0.23 |
| CR7-6 | WS6 | 0 | 7.24 | 48.20 | 0.471 | 0.134 | 5.19 | 2.69 | 0.85 | 0.19 | 0.11 | 0.72 | 0.03 | 0.76 |
| CR7-6 | WS6 | 3 | 6.94 | 44.3 | 0.344 | 0.089 | 1.96 | 0.7 | 1.24 | 0.05 | 0.02 | 0.00 | 0.00 | 0.94 |
| CR7-6 | WS6 | 6 | 6.59 | 37.4 | 0.056 | 0.023 | 0.79 | 0.24 | 3.47 | 0.07 | 0.06 | 0.10 | 0.00 | 0.65 |

Appendix 26 (continued): November Sampling Event (5 of 5) 2005

| Site Designation | Sampler ID | Sampler Gage | pH | Conductivity (us/cm) | TSS (g/L) | TOSS (g/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | TP (mg/L) | SRP (mg/L) | NH₃-N(mg/L) | NO₃ (mg/L) | TN (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Current River @ 106 Bridge | | Grab | 9.49 | 108 | 0.084 | 0.025 | 8.86 | 7.50 | 0.89 | 0.02 | 0.02 | 0.01 | 0.03 | 0.26 |
| SHOP HOLLOW | | Grab | 7.25 | 85 | 0.016 | 0.014 | 10.07 | 7.55 | 1.00 | 0.03 | 0.01 | 0.02 | 0.03 | 0.14 |
| Shop Hollow 2 | | grab | 7.09 | 127.5 | 0.146 | 0.033 | 8.33 | 5.66 | 0.69 | 0.01 | 0.01 | 0.02 | 0.06 | 0.51 |